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Very short functionalized carbon nanotubes for membrane applications ☆

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ABSTRACT

The cutting and functionalization of carbon nanotubes is described, applying a single-step ball-mill based process. Very short carbon nanotubes bearing primary amine functions were produced, characterized and incorporated in polymeric membranes. The gas separation performance of the composite membranes was tested.

1. Introduction

A single wall carbon nanotube (SWNT) is a cylindrical tubule obtained by rolling a graphene sheet into a cylinder, so that equivalent points do superimpose, followed by its closure at the superimposing points [1]. A multiwall carbon nanotube (MWNT) is obtained by packing several SWNT like a Russian doll, maintaining a typical graphite interlayer distance of 0.34 nm between the SWNT. The smallest MWNT contains only two walls and it is called double wall carbon nanotube (DWNT). It represents the perfect compromise between the narrower SWNT that has poor chemical and mechanical resistance and the thicker MWNT which is chemically and mechanically very resistant. In fact, the inner wall of a DWNT, if defect-free, is enough to ensure the remarkable electrical, mechanical and thermal properties of carbon nanotubes (CNT). The outer wall of a DWNT can ensure the chemical resistance and can accommodate surface defects such as holes and discontinuities without affecting drastically its properties. Moreover, while any functionalization will introduce defects on a SWNT and hence lower its remarkable electrical, mechanical and thermal properties, the functionalization will take place on the outer wall of a DWNT, thus maintaining its inner wall nanotube structure unaffected.

Experimental results have shown that the addition of low concentrations of CNT in polymer matrices can significantly enhance the mechanical strength of the polymer materials [2]. Theoretical calculations also predict very high gas separation selectivity for CNT of very small inner diameter (<10 Å) [3,4]. Nevertheless, up to now most of the experimental tests were performed using CNT of inner diameter >10 Å and only permeability increases could be observed [5]. Moreover, some authors attribute the CNT-enhanced gas permeability to the formed nanogaps surrounding the CNT [6]. Hence, to improve the selectivity of the polymer material towards CO_2, the outer wall of the CNT should be adequately functionalized, e.g. by the introduction of amines.

In the present work, very short MWNT with lengths lower than the membrane thickness were produced by ball-milling. As a result, the nanotubes average lengths were shortened, down to 300 nm for MWNT (5 to 10 walls) and to 50 nm for DWNT, respectively. The MWNT were also functionalized by the introduction of NH_2 functions in order to improve the selectivity towards CO_2 in the gas separation membranes based on MWNT. In fact, the cutting and functionalization was performed in a single step, using ball-milling [7–9] in the presence of NH_3 as reacting gas.

2. Experimental

Two types of purified carbon nanotubes, produced by the catalytic carbon vapor deposition (CCVD) method — MWNT (NC-3100) and DWNT (NC-2100) — were purchased from Nanocyl SA and used as starting materials for cutting and functionalization. The average inner/outer diameters of the MWNT and DWNT were 5/10 and 2.5/2.8 nm, respectively.

Carbon nanotubes powder (3.3 g) was introduced in the agate mortar of the ball-milling apparatus (Pulverisette 0, Fritsch) containing an agate bowl of 5 or 7 cm in diameter and the system was evacuated down to 0.01 mbar, using a primary vacuum pump. The reactant gas was NH_3 (N45 Air Liquide), which was introduced and kept at 1,2 bars during the ball-milling process, at an amplitude (vertical vibration intensity) of 1.2 or 3 mm. Finally, the system is evacuated again down to 0.01 mbar and then opened to air.

The ball-milling effect on the nanotubes was analyzed by transmission electron microscopy (TEM), using a Tecnai 10 (Philips) microscope. To prepare grids, 1 mg of sample was dispersed in 2 ml of ethanol, followed by 2 min sonication. Finally, a drop was deposited on a Cu/Rh grid, covered with formvar and the grid was dried at open air.

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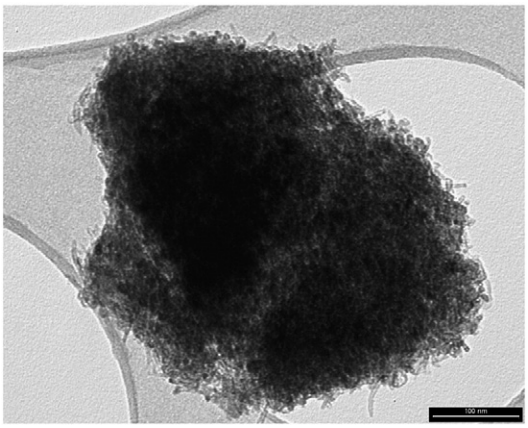

Fig. 1. Low magnification TEM image of short and functionalized DWNT-NH_2 produced by 32 h of ball-milling in the presence of ammonia.

X-ray photoelectron spectroscopy (XPS) was carried out on an SSX-100 spectrometer using monochromatized X-ray Al K_α radiation to determine the surface composition of the nanotubes. The nanotubes powder was mechanically spread on a conductive Cu tape (Scotch 3M) and the spectra were recorded at a fixed take-off angle of 35°. The core line levels (C 1s, O 1s and N 1s) were referenced with respect to the C 1s energy characteristic of sp^2 species conventionally set here at 284.6 eV.

3. Results and discussion

We describe hereafter the full cutting and functionalization process applied to DWNT. Afterwards, a sample of short MWNT-NH_2 produced under optimized conditions is described, followed by its use in membrane production for permeability tests.

3.1. Production of very short DWNT-NH_2

The cutting and functionalization of DWNT was achieved using the ball-milling process described, using a 7 cm agate bowl, vibrating at an amplitude of 1.2 mm. The milling time was screened from 1 to 32 h. After a given milling time, the process was interrupted, the system was evacuated and then opened to air for a 50 mg sample extraction. Afterwards, the system was evacuated, the NH_3 pressure was reestablished and the milling was resumed for a given time.

The different samples were characterized by TEM and by XPS. According to the TEM analysis, after 1 h of ball-milling, the DWNT are shortened but many long and thick bundles do remain, together with very short nanotubes. After 2–4 h of milling, the abundance length and thickness of the bundles decrease progressively. On the samples milled for 8 h, long bundles of DWNT are not observed any more. The sample milled for 16 h is made of only short nanotubes. Finally, after 32 h of milling, only short nanotubes of about 50 nm are observed, together with some rare long ones, up to 500 nm. The sample also contains abundant very short nanotubes, the shortest being of about 10 nm (Fig. 1).

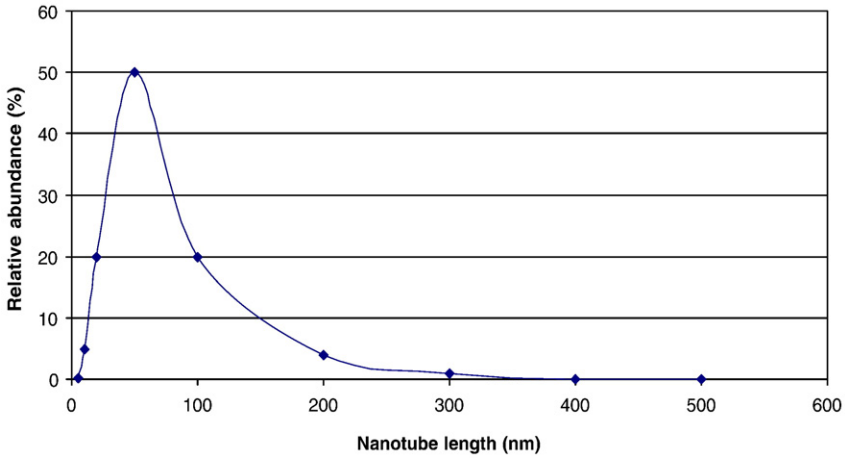

Fig. 2. Approximate length distribution curve of the DWNT milled for 32 h in the presence of 1.2 bar of ammonia.

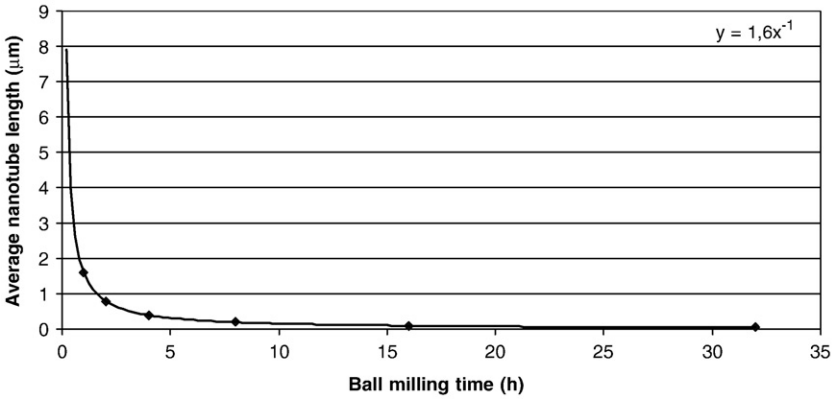

Fig. 3. Average DWNT length evolution as a function of the ball-milling time.

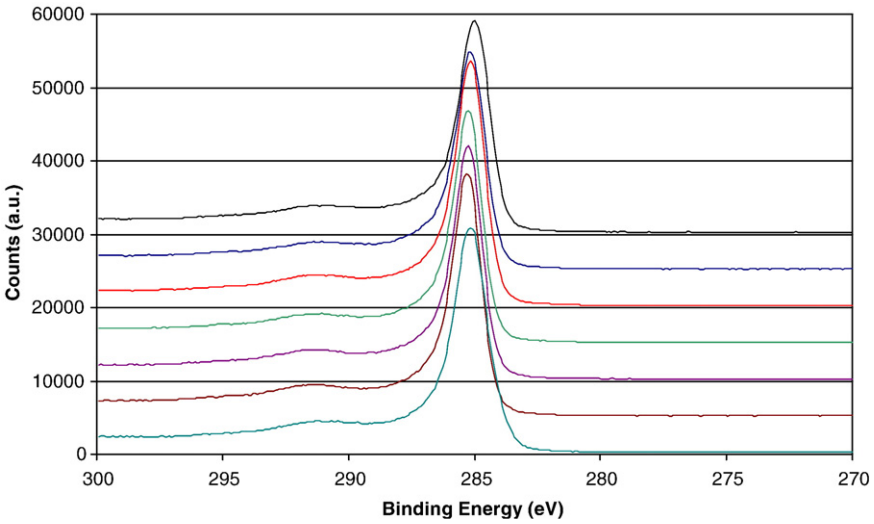

Fig. 4. Carbon (C 1s) XPS spectra of DWNT samples, after given milling times in the presence of ammonia. Milling times upwards: 0 h, 1 h, 2 h, 4 h, 8 h, 16 h and 32 h.

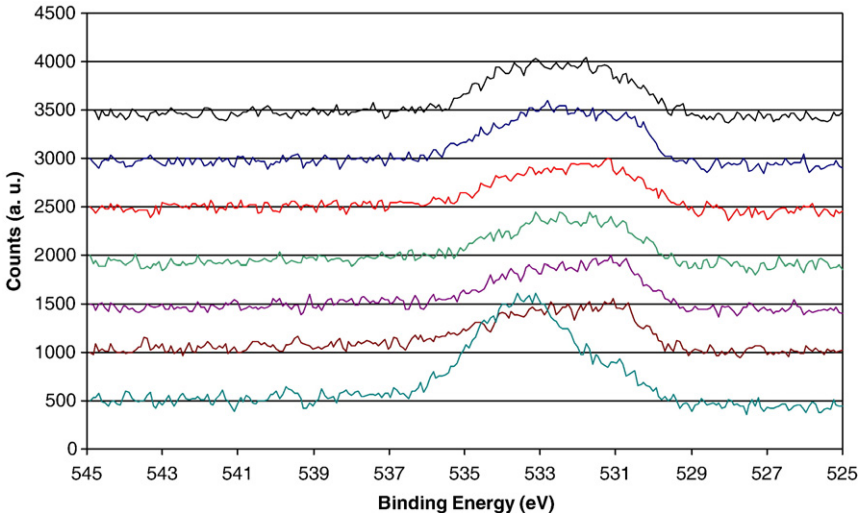

Fig. 5. Oxygen (O 1s) XPS spectra of DWNT samples, after given milling times in the presence of ammonia. Milling times upwards: 0 h, 1 h, 2 h, 4 h, 8 h, 16 h and 32 h.

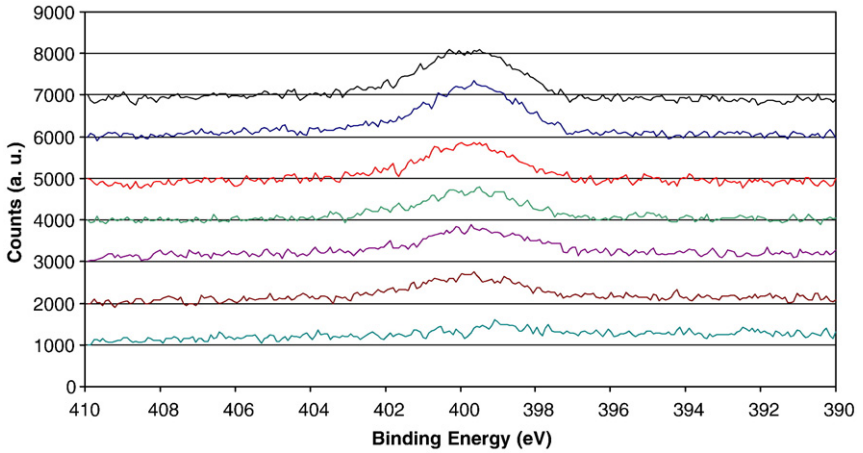

Fig. 6. Nitrogen (N 1s) XPS spectra of DWNT samples, after given milling times in the presence of ammonia. Milling times upwards: 0 h, 1 h, 2 h, 4 h, 8 h, 16 h and 32 h.

Table 1
Nitrogen and oxygen content of the DWNT samples, determined by XPS.

Milling time (h)	0	1	2	4	8	16	32
N (at.%)	0	0.9	0.9	1.0	1.0	2.2	1.9
O (at.%)	1.3	1.2	1.2	1.2	1.1	1.6	1.5

The approximate length distribution curve of the DWNT milled for 32 h in the presence of 1.2 bar of ammonia is represented in Fig. 2. It was established from the analysis of 50 to 100 TEM pictures of each sample. As seen in Fig. 2, the nanotubes length distribution curve is monomodal.

The average DWNT length evolution as a function of the ball-milling time is represented in Fig. 3. As seen in that figure, the nanotubes length decrease follows inverse time decay.

The short DWNT-NH_2 samples were also analyzed by XPS to quantify and identify the nature of the nitrogen and oxygen atoms of the samples. The carbon (C 1s) oxygen (O 1s) and nitrogen (N 1s) XPS spectra are represented in Figs. 4–6, respectively.

On the carbon (C 1s) spectra, Fig. 4, very little modification is observed as a function of the milling and functionalization time. Such a small variation is due to the very small extent of the functionalization, which is within 1 to 2 at.% (Table 1).

On the oxygen (O 1s) spectra, Fig. 5, a modification is observed after the first milling hour. It is possibly due to the conversion of the carboxyl to amide functions. Afterwards, there is nearly no variation up to 8 h of ball-milling. For the samples milled for 16 and 32 h, an increase of the oxygen atomic % is observed (Table 1), possibly due to the quenching of the free radicals in the samples when exposed to the open air.

On the nitrogen (N 1s) spectra, Fig. 6, the progressive introduction of nitrogen can be observed as a function of the milling and functionalization time. Again, like for the oxygen spectra (Fig. 5), a more important increase of the nitrogen atomic % is observed for the samples milled for 16 and 32 h (Table 1).

The nitrogen and oxygen content of the DWNT samples, determined from the general XPS spectra, is summarized in Table 1.

Hence, very short DWNT-NH_2, of an average length of 50 nm and containing ca. 2 at.% of nitrogen was produced, applying a ball-milling time of 32 h. As seen in Table 1, the sample is also partially oxidized by the process, the final sample revealing ca. 1.5 at.% of oxygen.

3.2. Production of short MWNT-NH_2

The cutting and functionalization of MWNT was achieved using the ball-milling process described, applying a 5 cm agate bowl, vibrating at an amplitude of 3 mm. The milling time was screened from 1 to 120 h, but only the final product (Fig. 7) is considered in the present work.

The average carbon nanotube length in the short and functionalized MWNT-NH_2 sample is 300 nm (Fig. 7).

Concerning the functionalization, a nitrogen content of 1.9 at.% was measured by XPS for the short and functionalized MWNT-NH_2 sample. The oxygen content of the sample was 2.0 at.%. The latter sample was used for membrane production and, the membranes permeability and selectivity towards CO_2, versus N_2, were measured.

3.3. Application of short MWNT-NH_2 for membrane production

PEBAX® [10] is one of the best copolymers providing reasonable selectivity for CO_2 over N_2, and high permeability for CO_2. PEBAX® 1074 was chosen as membrane matrix material for the carbon nanotube based membranes. The carbon nanotubes used were short and functionalized MWNT-NH_2. Hence, PEBAX® based dense membranes containing 0.5, 1.0 and 2.0 wt.% of MWNT-NH_2 were produced, characterized by TEM after microtome cutting (Fig. 8) and their gas separating performance was tested.

Fig. 8 contains two TEM pictures of the membrane containing 0.5 wt.% of short and functionalized MWNT-NH_2. The left picture shows a cracked membrane containing nanotubes. The right picture is a higher magnification where the nanotubes dispersed in the membrane can be observed.

Concerning the effect of MWNT-NH_2 on the membrane performance, the results of the single gas permeation experiments performed show that the addition of 0.5 wt.% of nanotubes does have a significant positive effect on the CO_2 permeability (40% increase), but does not influence the selectivity.

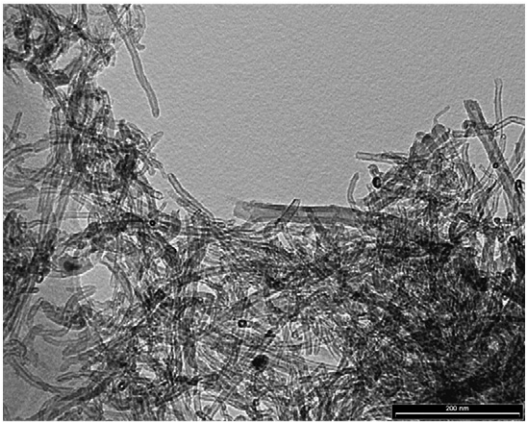

Fig. 7. Low magnification TEM image of short and functionalized MWNT-NH_2 produced by 120 h of ball-milling in the presence of ammonia.

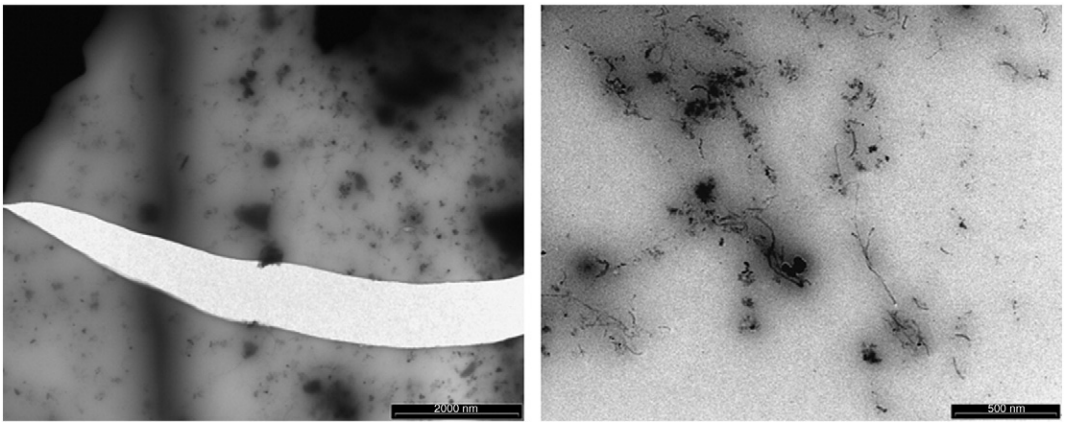

Fig. 8. Low magnification TEM pictures of the PEBAX® based membrane containing 0.5 wt.% of short and functionalized MWNT-NH_2.

4. Conclusion

Very short DWNT-NH_2, made of short nanotubes of an average length of 50 nm, was produced. The product also contains some rare long nanotubes, up to 500 nm, and abundant very short nanotubes, the shortest being of about 10 nm. The nitrogen atomic percent introduced on the nanotubes was ca. 2.

Short MWNT-NH_2, made of short nanotubes of an average length of 300 nm and containing ca. 1.9 at.% of nitrogen, was also produced. The latter sample was successfully introduced in PEBAX® polymer membranes and a 40% permeability increase was observed compared to the non modified PEBAX® membrane.

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