

Preparation and Characterization of Carbon Nanotube/Polyacrylonitrile Composites**

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The discovery of carbon nanotubes (NT) by Iijima^[1] in 1991 attracted scientific and technological interest worldwide. NT exhibit remarkable intrinsic properties such as high mechanical strength,^[2] and structurally dependent electrical conductivity^[3,4] and thermal conductivity,^[5] which make them very interesting. It is also believed that the incorporation of carbon nanotubes in polymer matrices should lead to composites with unique properties.^[6] Accordingly, many polymers are presently being investigated as host matrices for carbon nanotubes and the resulting composites are being assessed for a number of properties: flame-retardant behavior,^[7] electrical and optical conductivity,^[8,9] and electrostatic charging behavior.^[10]

Recent experimental^[2,11,12] and theoretical^[13,14] studies have demonstrated that individual nanotubes have extremely high Young's modulus (about 1.2 TPa), good stiffness, and flexibility. Moreover, mechanical properties (bending modulus) depend on the quality^[15] and the diameter^[16] of the multiwalled nanotubes. It is thus tempting to use NT for mechanical reinforcement and to obtain new materials with unusual mechanical properties. However, the ultimate performance of such materials is expected to depend strongly on their ability to transfer load from the host matrix to the nanotubes.^[10,17] This ability is directly related to the possibility of achieving homogeneously dispersed nanocomposites and thus to the nature of the interactions developing between the nanotubes and the polymer chains.

Various techniques are used to disperse nanotubes in polymer matrices. The most straightforward is direct mixing, but this does not always give homogeneity because of the frequent lack of compatibility between the polymer chains and the NT.^[18] Ultrasonic activation can be used, but it often takes several hours to achieve a satisfactory dispersion.^[19] Surfactants are also used to modify the surface tension at the interface between the NT and the polymer chains to improve interfacial bonding.^[20] In-situ polymerization^[21] of the polymer on NT or surface functionalization of the NT^[22] have also been investigated. These examples, and others not cited here, show that fabricating homogeneous polymer nanocomposites with NT remains a major challenge very much dependent on the chemical nature of the polymer host.

In this communication we report our attempts to disperse multiwalled carbon nanotubes (MWNT) in a polyacrylonitrile

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(PAN) matrix, which, to our knowledge, has not been investigated before. Dispersion of the NT was attempted by direct application of ultrasonic energy to a solution of PAN in dimethylformamide, a choice based on the fact that NT alone are best dissolved in this solvent.^[23,24] Our next aim was to assess the properties of MWNT/PAN composites in line with recent works on the effects of solid particulates on the structure and mechanical properties of coal-tar based C-C composites.^[25]

After a short presentation of the characterization tools, the synthesis, purification, and characterization of the MWNT are described. Preparation and characterization of the MWNT/PAN composites are also described and this communication concludes with a brief outlook to the future.

The combined use of PIXE (proton induced X-ray emission) and PIGE (proton induced γ -ray emission) techniques allowed us to quantify the elements present in the nanotube powder. To check the amounts of retained contaminants (F, V, Mn, Co, etc.) in the nanotubes, measurements were performed using ALTAIS, the new Tandetron accelerator 2 MV terminal at the LARN laboratory of the University of Namur. In the non-vacuum PIXE/PIGE set-up, an incident proton beam of 3.2 MeV crossed a thin Al foil (10 μm thick) before reaching the sample situated at a distance of 1 cm.^[26] The characteristic X- and γ -rays induced in the sample were detected by Si(Li) and Ge(Li) detectors, respectively. The radiation was quantified by comparing with standard samples.^[27] The presence of V, Mn, and Co was determined by PIXE and F by PIGE.

X-ray diffraction (PW3710 BASED, Philips, Cu K α radiation: 1.5418 \AA , CMS laboratory of the University of Namur) experiments were carried out on both the isolated MWNT and the composite films. The XRD patterns were recorded in the range 15–50° (2θ) with a step size of 0.04° and a time per step of 1 s. The diffractograms were analyzed with diffraction software (PC-APD) using a smoothing factor of 2.

X-ray photoelectron spectroscopy or XPS (SSX-100, monochromatized AlK α radiation, 1486.6 eV, LISE laboratory of the University of Namur) was used to establish the surface elemental composition and to assess the chemical environment of the detected elements for both the MWNT alone and the composite films. Photoelectron spectra of the samples 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 sp² species^[28] and conventionally set here at 284.6 eV. In the case of the MWNT alone, the powder was mechanically spread on a conductive Cu tape (Scotch 3M). The thickness of the resulting “MWNT film” was greater than 10 nm because no trace of Cu could be detected. For the composite films, an electron flood gun (energy of a 1.0 eV) was used to reduce charging of the sample.

The morphology and structure of the MWNT and the composite films were studied by transmission electron microscopy (TEM) with JEOL 200 CX (high resolution) and Philips CM 20 (low resolution) instruments of the Unité Interfacul-

taire de Microscopie Electronique of the University of Namur. For analysis, the MWNT samples were prepared by sonicating about 1 mg of the nanotube powder in 10 mL ethanol. A few drops of the resulting suspension were put onto a holey-carbon TEM grid. In the case of the composite samples, the films were cut into very thin slices (about 80 nm) by an ultramicrotome. Then these slices were deposited onto a conventional TEM grid.

The multiwalled nanotubes used in this work were produced by catalytic decomposition of hydrocarbon.^[29] The catalyst obtained by the impregnation method,^[30,31] contained 2.5 wt.-% cobalt and 2.5 wt.-% vanadium supported on zeolite NaY. The zeolite NaY was used to obtain a good dispersion of the metal particles in the catalyst. The synthesis was carried out in a fixed-bed flow reactor at 700 °C for a reaction time of 60 min. For each synthesis, a quartz boat containing about 1 g of catalyst was placed at the center of the reactor. Acetylene and nitrogen were used as carbon source and gas carrier. During the reaction, the flows were fixed at 30 mL min⁻¹ for acetylene and 300 mL min⁻¹ for nitrogen (gas flows measured at STP conditions). The resulting powder was a mixture of MWNT, amorphous carbon, zeolite NaY, and metallic particles. The purification of the MWNT was done in two steps. First, an aqueous solution of hydrogen fluoride (HF, 48–50 %) was used to remove the zeolite support and the catalytic particles. Then, elimination of the amorphous carbon was achieved by oxidation of the powder with potassium permanganate in acidic solution (H₂SO₄, 2 M).^[31] At the end of these two steps, the carbon nanotubes were dried at 120 °C for 12 h and ground into a fine powder for composite preparation.

After the purification step, the MWNT were analyzed by various techniques. First, PIXE/PIGE analyses were done. Figure 1 represents the PIXE spectrum of the sample. The spectrum exhibited only four peaks corresponding to the K α and K β lines of Mn (K α : 5.90 keV and K β : 6.49 keV) and Co (K α : 6.93 keV and K β : 7.65 keV). Moreover, the analysis did not reveal the presence of V, which should have appeared at energies of 4.95 keV (K α) and 5.95 keV (K β). The PIGE analysis, not shown here, revealed only the presence of F. Quantification of these elements indicated 100 ppm of F, 730 ppm of Mn, and 760 ppm of Co. In conclusion, cobalt, used as catalytic particles, was less efficiently removed than the vanadium particles by HF treatment. The presence of Mn and F stemmed from the reagents used during purification. However, all these contaminants (F, Mn, and Co) represented less than 1 wt.-% of the carbon nanotube powder.

The XRD pattern (Fig. 2) of the MWNT sample revealed the presence of two peaks at 25.8 and 42.8 ° corresponding to the interlayer spacing (0.34 nm) of the nanotube (d_{002}) and the d_{100} reflection of the carbon atoms, respectively, in good agreement with the literature.^[32] The asymmetry of the band at 42.8 ° was due to the turbostratic nature of the nanotubes. Moreover, the XRD spectrum corroborated the high purity of the nanotube samples observed in the PIXE/PIGE analysis

since no diffraction peak characteristic of the catalytic particles was observed. Note, however, that the same XRD pattern would have been acquired in the case of a graphitic product. Consequently, this analysis alone was insufficient to demonstrate the quality of the carbon nanotubes.

The XPS survey spectrum (Fig. 3a) of the purified MWNT revealed the presence of only carbon and oxygen. The relative atomic concentrations of carbon and oxygen were 87 and 13 % respectively. The XPS spectra of the C1s and O1s core levels are shown in Figure 3. The C1s core level (Fig. 3b) can be decomposed into five contributions appearing at 284.6, 285.3, 286.2, 287.2, and 288.9 eV. The decompositions were obtained using an asymmetric peak analogous to that observed for graphite (284.6 eV) and four Gaussian peaks centered at 285.3, 286.2, 287.2, and 288.9 eV according to literature.^[33] The main peak at 284.6 eV was assigned to sp^2 -hybridized graphite-like carbon atoms and to sp^2 carbon atoms bound to hydrogen. The peak at 285.3 eV originated from sp^3 -hybridized carbon atoms as in diamond-like carbon. Peaks at 286.2, 287.2, and 288.9 eV were typical of carbon atoms bound to one oxygen atom by a single bond (e.g., alcohol, ether), by a double bond (e.g., ketone, aldehyde), and to two oxygen atoms (e.g., ester, carboxylic acid), respectively. At 291.0 eV there was the expected shake up feature typical of aromatic structures.^[34] The C 1s core level XPS spectrum of the MWNT powder obtained after only the first step of purification (i.e., without oxidative treatment with potassium permanganate) is shown in Figure 3d. In that case, the same five components were used and the only changes were in the relative percentage of each contribution, as shown in Table 1.

After purification, a reduction of the sp^2 species with an increase of the sp^3 species and carbon atoms present in functions such as carboxylic acid were observed. This was in agreement with the fact that potassium permanganate in acidic solution leads to the oxidation of carbon nanotubes by preferentially creating carboxylic functions. The O1s peak (Fig. 3c) was decomposed into three components appearing at 531.7, 533.0, and 534.0 eV and corresponding to oxygen atoms bound to carbon atoms in functions like alcohol ($C-OH$), ketone ($C-O-C$), and carboxylic acid ($COOH$ and/or $-OC-O-CO-$) respectively.^[34]

TEM observations revealed unambiguously the presence of long (several micrometers) individual MWNT. Moreover, various types (helicoïdal, linear, etc.) of MWNT were observed (Fig. 4a). After purification, the amorphous carbon islands were completely removed from the sample and only a small quantity of amorphous carbon was present at the surface of the MWNT (Fig. 4b). We observed that MWNT presented average inner and outer diameters of 4 and 13 nm, respectively. With an intertube distance of 3.4 Å, this corresponded to 13 graphitic layers.

The preparation of the composite films was done in three steps. First, a solution of polyacrylonitrile (PAN) (2.5 wt.-%) was obtained by dissolving the PAN in dimethylformamide (DMF) at 70 °C with stirring. Then the multiwalled carbon

nanotubes were added to the solution at room temperature and mixed by two methods: i) the mixture was placed in an ultrasonic bath for 6 h (Branson 1210), or ii) an ultrasonic head (Branson sonifier 250) was introduced in the solution for 2×15 min. After that, DMF was evaporated using a high power lamp to produce the composite films; 4 mL of the solution was used to obtain composite film (50 μm thick). The estimated concentration of the nanotubes was 4 wt.-% with respect to the polymer concentration.

First, TEM observations at low resolution were used to assess the degree of dispersion of the carbon nanotubes in the polymer matrix. Then, the composite films were analyzed by XRD and XPS techniques.

As already mentioned, two methods were tried for dispersing the nanotubes in the solution of PAN: 6 h in an ultrasonic bath or 2×15 min of ultrasonic head. TEM observations of these two types of samples revealed some differences in the homogeneity of the nanotube dispersion. Figure 5 represents two low-resolution TEM images of composite films prepared using the ultrasonic bath (Fig. 5a) and the sonication head (Fig. 5b). In the first case, some aggregates of MWNT appeared as well as a few isolated nanotubes. In the second case, all the nanotubes were more homogeneously dispersed in the matrix. From these observations, we can conclude that the second method allows one to obtain a good dispersion of the nanotubes in the polymeric matrix.

Figure 6 shows the XRD patterns of the MWNT alone, the pure polyacrylonitrile, and the composite films with 4 and 25 wt.-% of nanotubes. In the case of pure polyacrylonitrile, the spectrum showed a sharp intense peak at 16.7° and a small diffraction peak at 29.0° . The first peak corresponded to the lateral repeat distance or Bragg spacing and was identified as the (100) diffraction of the hexagonal lattice.^[35] The second peak corresponded to the second-order diffraction of peak 1.^[35] The XRD pattern of the composite film showed mixing of the peaks appearing for the pure MWNT and pure polyacrylonitrile samples. Moreover, the peaks assigned to the nanotubes in the composite increased when the charge of the nanotubes in the film increased. We concluded that the preparation method did not induce an alteration of the structure of the nanotubes and the polymer chains.

The survey scan XPS spectrum of a composite film with 4 wt.-% of carbon nanotubes shown in Figure 7 exhibited two intense and narrow peaks at 285.5 and 399.6 eV corresponding to C 1s and N 1s core levels, respectively. We observed also that oxygen was only present at trace level, as shown by the very weak intensity O 1s peak centered at 532.0 eV. The relative atomic concentrations of C, N, and O estimated from XPS were 78, 21, and 1 %, respectively. A detailed study of the individual peaks was not possible because of charging of the sample during the XPS analysis, which led to a shape deformation of the peak. In the case of C 1s, the contribution of the nanotubes and the polymer could not be identified and separated. In pure polyacrylonitrile, there are three carbon atoms for one nitrogen atom in the repeat unit. As expected,

the addition of carbon nanotubes revealed an increase of carbon percentage relative to nitrogen.

In this communication, we report a method for obtaining a homogeneous dispersion of multiwalled carbon nanotubes in polyacrylonitrile films. Dispersion of the carbon nanotubes was realized by direct application of ultrasonic energy to a solution of PAN in dimethylformamide. Two methods were used: an ultrasonic bath or an ultrasonic head. In the second case, a homogeneous dispersion of the NT in the polymer matrix was achieved more rapidly. Moreover, our analysis demonstrated the non-alteration of the nanotubes and polymer structures after all the steps of composite fabrication.

This work opens the way to studying the properties of these new composites by various methods. Electrical and thermal conductivity and mechanical properties will be investigated and the influence of the amount of carbon nanotubes in the composite will be evaluated. This will be done by comparing the properties before and after the addition of the nanotubes. Moreover, various modifications of the MWNT/PAN composites will be made to assess their potential as materials with new or improved properties.

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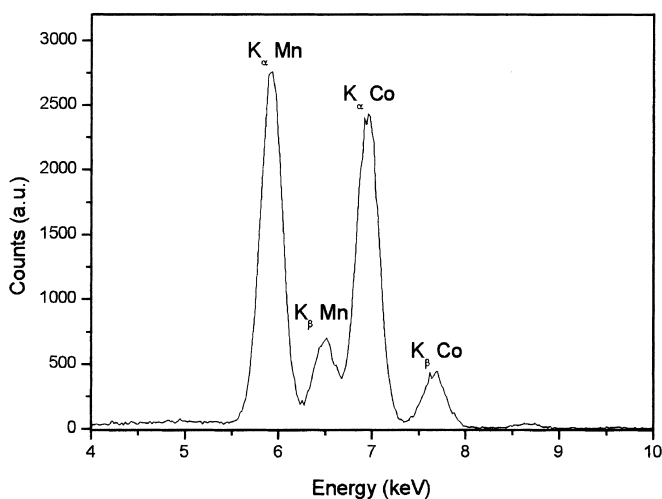


Fig. 1. PIXE spectrum of the purified MWNT.

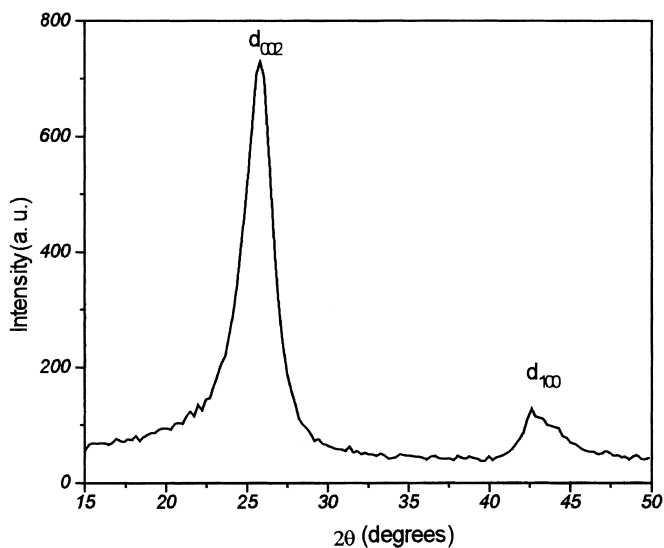
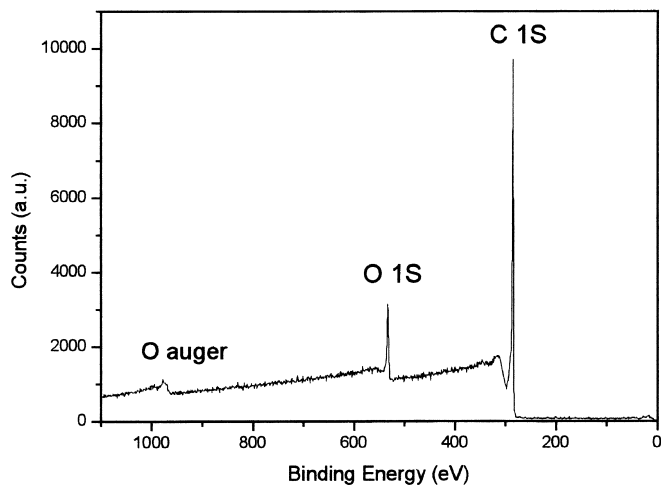
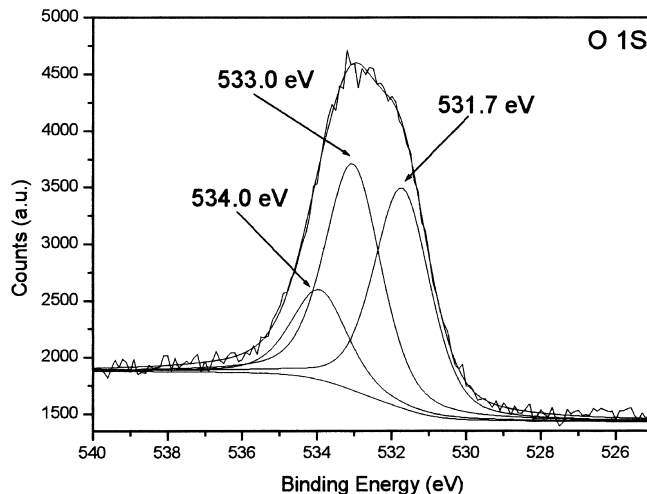


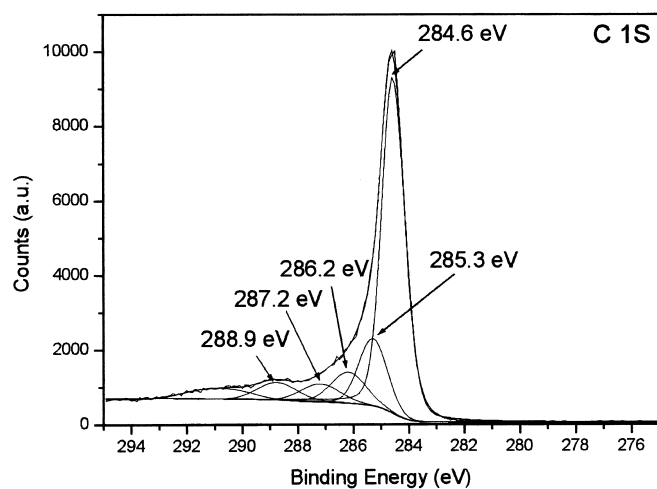
Fig. 2. Powder X-ray diffractogram of the purified MWNT.



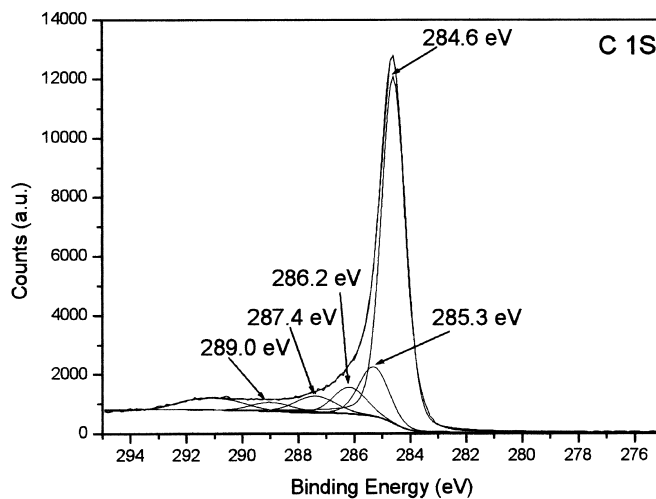
(a)



(c)

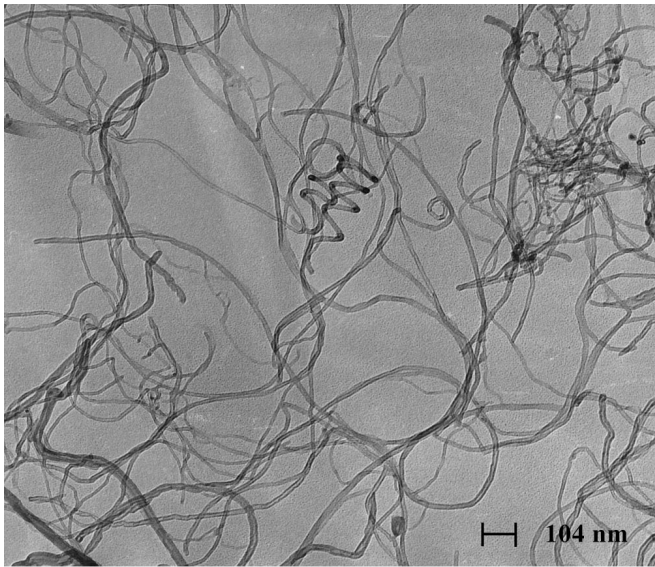


(b)

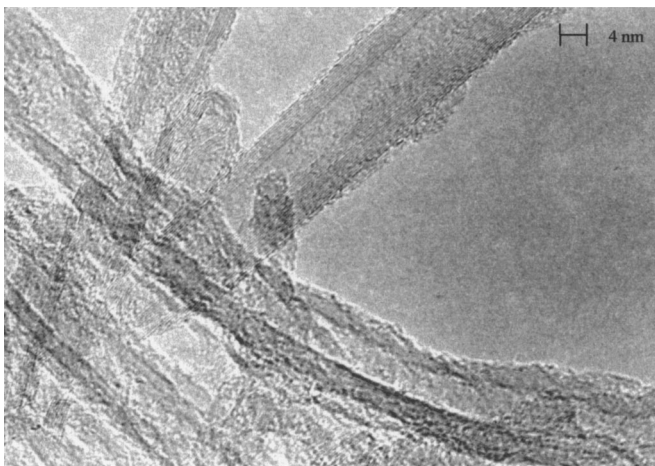


(d)

Fig. 3. a) Survey XPS spectrum; b) and XPS spectra of the C 1s; c) O 1s core levels of the purified MWNT. d) XPS spectrum of the C 1s core level of the MWNT after only the first step of the purification.

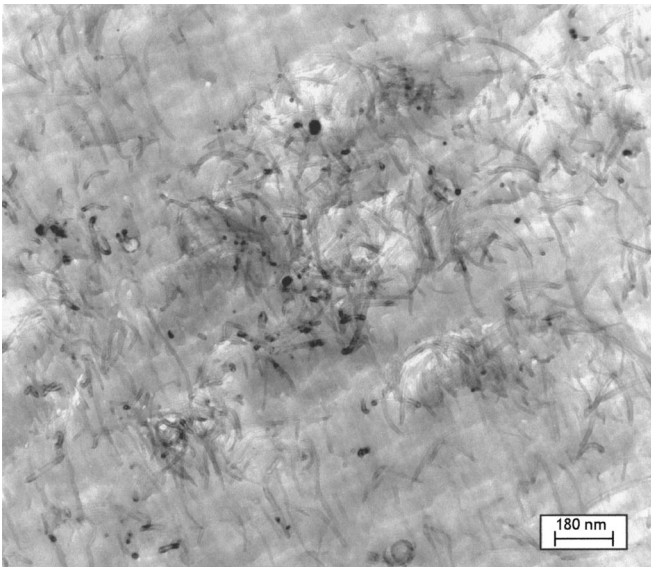


a)

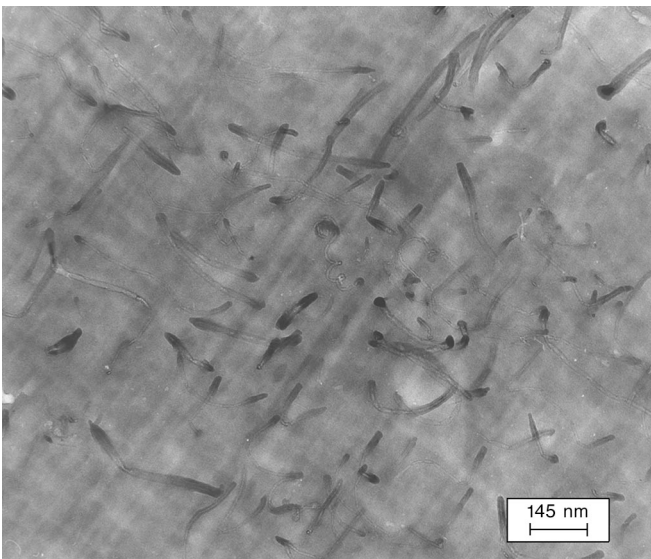


b)

Fig. 4. a) Low and b) high resolution TEM images of the purified MWNT.



a)



b)

Fig. 5. Low resolution TEM images of composite films prepared using: a) the ultrasonic bath for 6 h; b) the sonication head for 2×15 min. The charge of the MWNT is 4 wt.-% with respect to the polymer concentration.

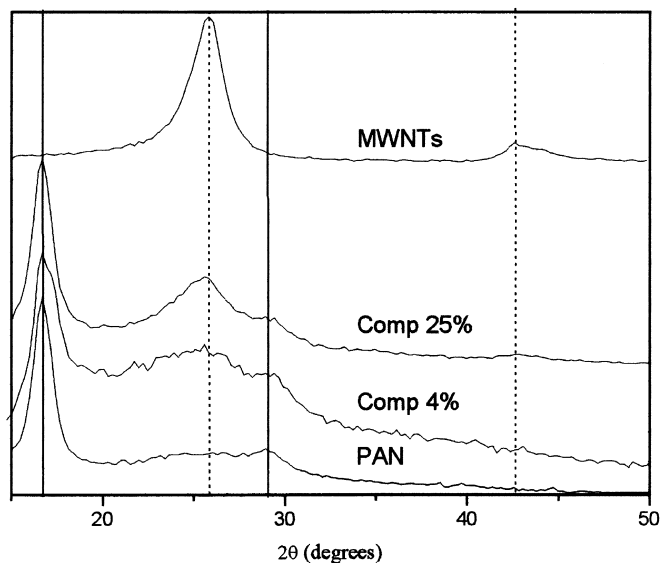


Fig. 6. Powder X-ray diffractograms of the MWNT alone, of pure polyacrylonitrile and composite films charged with 4 and 25 wt.-% of nanotubes.

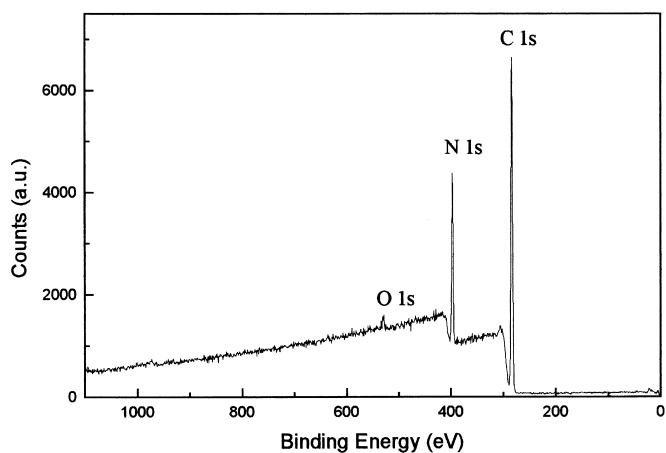


Fig. 7. Survey XPS spectrum of a MWNT/PAN composite film. The charge of carbon nanotubes is 4 wt.% with respect to the polymer concentration.

Table 1. Relative percentages of the five XPS components of carbon atoms in the MWNT powder after the first and second purification steps.

MWNT	sp ² [%]	sp ³ [%]	-C-O [%]	-C=O [%]	-COO- [%]
After the first purification step	74	12	7	5	2
After the second purification step	67	14	8	5	6