

SYNTHESIS AND INVESTIGATION OF FLUORINATED CARBON MULTI-WALLED NANOTUBES

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Introduction

Fluorination is one of effective methods for modification of carbon materials to improve the interphase adhesion between filler and polymeric matrix in nanocomposites. The products of fluorination can differ both by the content of fluorine and by bond strength C-F. In this report we present results of investigation of fluorination products of carbon multi-walled nanotubes (MWNT).

Results and discussion

MWNT were produced by arc-discharge evaporation of spectral graphite rods $\varnothing 10 \times 170$ mm (total percentage impurity less than 8×10^{-4} wt.%) [1,2]. At helium pressure of 500 Torr, dc current of 130 A and voltage of about 23 V the yield of MWNT (recovered from core of cathodic deposit) achieved 20–24%. A SEM image demonstrates the bundles of MWNT, multilayer particles and amorphous carbon (fig. 1) The outside diameter of MWNT is 5–50 nm, the length – ~ 1 micron.

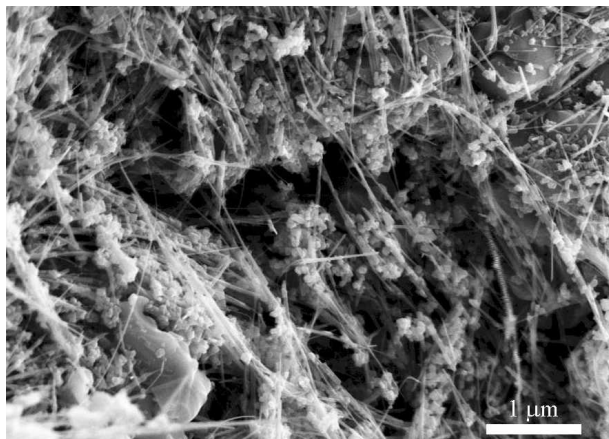


Fig. 1. SEM image of initial MWNT

The oxidative thermogravimetry allowed us to ascertain that to purify MWNT from amorphous carbon the heating up to 700°C under air is required. After this treatment nanotubes and graphitic fragments (mass ~ 60 %) remain in the solid phase.

Fluorination of as-prepared MWNT (columnar structure) was performed in a nickel reactor at a temperature of about 420°C in a flow of gaseous fluorine diluted with nitrogen at the ratio of 1:10.

Gaseous fluorine was produced by electrolysis of acidic potassium trifluoride $\text{KF} \cdot 2\text{HF}$ and contained 3% HF. Depending on the time of fluorination samples with the fluorine content from 10 up to 55 wt.% were obtained.

With increasing the fluorine contents the decrease in the intensity of main peaks is observed on a MWNT X-ray diffraction pattern. The profile of the reflection 10 is changed and a "shoulder" shifted towards lower angles is appeared. This evidences the increasing C–C bond length in graphene layers. However the reflection 002 of initial MWNT is detected even for the sample F55% (fig. 2). Interlayer distances for a new graphite-like structure produced after fluorination achieve 0.46–0.48 nm that essentially exceeds those for initial structure (0.34 nm).

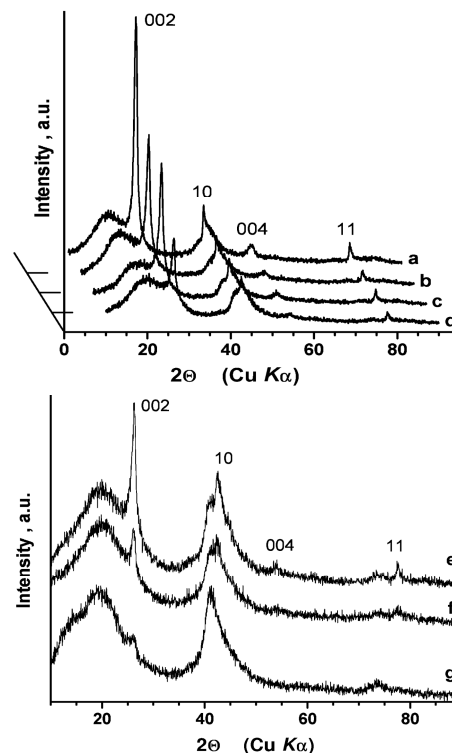


Fig. 2. X-ray diffractograms MWNT with different fluorine content (wt.%): a) 10; b) 15; c) 18; d) 25.4; e) 31; f) 39; g) 55

A typical oxidation thermogram of fluorinated MWNT is shown in fig. 3. It was found that weight loss takes place in 3 stages: up to 300°C – evolution of adsorbed gases, in the range

300-550°C – destruction of fluorinated material and evolution of gaseous fluorocarbons, more then 600°C – oxidation of the sample with the single maximum in a DTG curve.

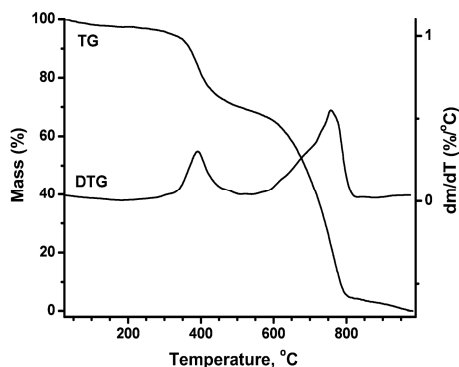


Fig. 3. Oxidation thermogram (in a flow of 5 vol% O₂/Ar) of fluorinated MWNT F25.4%, heating rate 5°C/min

In the IR spectrum of the sample with fluorine content 25.4 wt.% (F25.4%) the broad asymmetric absorption band is observed. This band can be represented as the sum of two Gaussian components with maxima at 1215 and 1145 cm⁻¹. With increasing the fluorine content (F55%) the position of basic peak shifts towards higher wavenumbers approaching to that for the composition C₂F (1240 cm⁻¹), and the intensity of the peak (relating to bonds C–F with higher ionic component) being reduced (fig. 4).

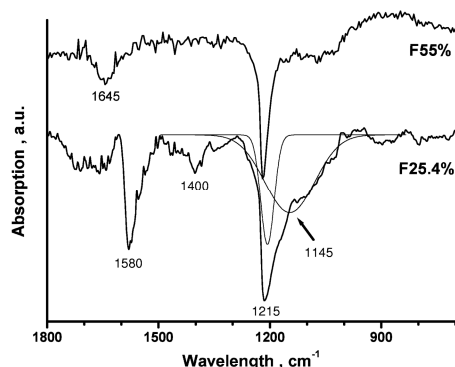


Fig. 4. IR spectra of fluorinated MWNT with the fluorine content of 25.4 and 55 wt.%

Fluorination increases the specific surface area from 15 m²/g for initial MWNT up to 50 and 120 m²/g for the samples F39% and F55%. Nitrogen adsorption-desorption isotherms of MWNT have hysteresis (fig. 5).

The volume of micropores of fluorinated MWNT is increased with increasing the fluorine content, mainly, because of increase in the quantity of pores with the diameters ranging in 1.5–2.0 nm (fig. 6).

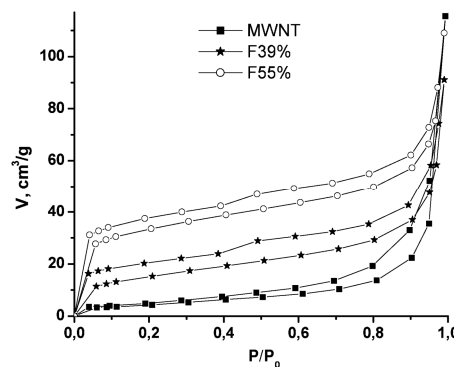


Fig. 5. Nitrogen adsorption-desorption isotherms at 77 K

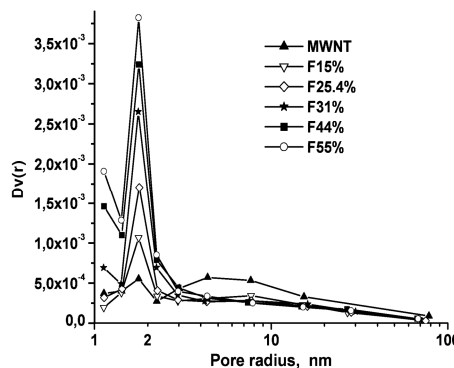


Fig. 6. Pore size distribution curves

Conclusions

The conditions are determined for the highest yield of MWNT of columnar structure produced at arc-discharge evaporation of graphite rods.

Fluorinated MWNT with the fluorine content of 10-55 wt.% are prepared. It was shown, that fluorinated MWNT have C–F bonds with different degree of ionicity and exhibit the interlayer distance of 0.46–0.48 nm.

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References

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