ELECTRICAL RESPONSE OF MULTIWALL CARBON NANOTUBES (MWCNT) “BUCKYPAPER” TO DEFORMATION

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PROCEDURE

Synthesis of polyurethane (PU). PU solution in dimethylformamide (DMF) was synthesized from 4,4’-methylenebis(phenyl isocyanate) (MDI) purchased from Bayer, Germany, the poly(3-methyl-1,5-pentanediol)-alt-(adic, isophtalic acid) polymer diol (PAIM, $M_n \sim 2.10^3$) purchased from Kuraray, Japan, and 1,4-butanediol (BD) purchased from BASF, Germany. PU was synthesized by “per partes” method [1] in molar ratio of monomers 9:1:8 at temperature 90°C for 5 hours. There was synthesized prepolymer from MDI and polymer diol (molar ratio 2:1) at the first step followed by addition of all BD in the second step and finally after one hour of polyaddition reaction the remaining MDI was added.

Electrospinning process. PU nanofibers were prepared using commercially available machine Nanospider (Elmarco s.r.o. Czech Republic) employing one rotational electrode with three crossways aligned cotton cords. The PU solution viscosity in DMF was adjusted to $\eta = 1.5$ Pas (which corresponds to PU concentration of about 13.5 wt.% and solution conductivity was adjusted by tetraethylammonium bromide to $\chi \sim 165 \mu$S/cm. Other experimental conditions were as follows: Relative humidity RH \sim 26 \%, temperature T \sim 26°C, electric voltage $U = 75 \text{kV}$, electric current $I \sim 24 \mu\text{A}$, distance between rotating and static electrode $L = 18 \text{ cm}$, electrode spin $R = 7 \text{ r/min.}$, speed of antistatic polypropylene nonwoven fabric collecting nanofibres $S = 0.16 \text{ m/min}$ [2].

MWCNT buckypaper. The MWCNT, acetylene type, purified, were supplied by Sun Nanotech Co. Ltd., China (diameter 10-30 nm, length 1-10 µm, purity >90% and volume resistance 0.12 $\Omega \cdot \text{cm}$ reported by supplier). The aqueous MWCNT paste was prepared using of 1.6 g of MWCNT and \sim 50ml of deionized water using a mortar and pestle. The paste was diluted by deionized water and SDS plus 1-pentanol were added. For adjusting pH = 10, the aqueous NaOH solution was used. The final concentration of nanotubes in dispersion were 0.3 wt. %, the concentration of SDS 0.1M and the concentration of 1-pentanol 0.14M. Then the dispersion was sonicated using Dr. Hielscher GmbH apparatus (ultrasonic horn S7, amplitude 88 µm, density of power 300 W/cm², frequency 24 kHz) for 2 hours and temperature reaching \sim 50°C.

The MWCNT aqueous dispersion was filtered thought polyurethane (PU) mesh and MWNT entangled network (buckypaper) was formed. After network washing by deionised water and methanol, the network was dried between two dry filter paper for a moment and then the one was gently peel off the PU filter and dried between iron plates at RT.
RESULTS

Figure 1 represents the PU filtering mesh. Part a) as produced and part b) after filtration of CNT dispersion and subsequent pealing off MWCNT entangled network. PU fibres are straight shaped with relatively smooth surface of submicron size having quite uniform diameter with average diameter 0.14±0.09 µm ranging between 0.05-0.39µm. The main pore size is around 0.2µm. In part B individual CNT tubes are visible in pores and attached on the surface of PU fibres.

![Fig.1 SEM micrographs of PU non-woven filtering membrane part a). Part b) represents the same membrane just after pealing off MWNT network.](image)

Figure 2, part a), represents prepared MWNT network and part b) the detailed SEM analysis of its surface. The network is formed by randomly entangled nanotubes. The porous structure of network is uniform with an average pores size around 40 nm. The relative network shrinkage during drying was measured to be about 7.1 %. The porosity, ε, was calculated from equation, $1 - \varepsilon = \frac{\rho_{\text{CNT}_p}}{\rho_{\text{MWCNT}}}$, where $\rho_{\text{CNT}_p}$ represents apparent density of the network, $\rho_{\text{CNT}_p} = 0.56±0.03$ g/cm$^3$, and $\rho_{\text{MWCNT}}$ density of carbon nanotubes. The density of carbon nanotubes was determined

![Fig. 2 a) Sample of CNT entangled network (diameter 75 mm, thickness 0.15 mm), b) Micrograph of randomly entangled carbon nanotubes taken on a SEM.](image)
\( \rho_{\text{MWCNT}} = 1.72 \text{ g/cm}^3 \) which is very close to value 1.8 g/cm\(^3\) theoretically evaluated for MWCNT [4]. This value of density serves the value of CNTp porosity, \( \varepsilon = 0.67 \pm 0.02 \) very similar to value usually published for buckypaper made of unfunctionalised multi-walled carbon nanotubes, 0.79-0.87 [5]. The electrical conductivity of the network was measured by four probe method what yielded the value (2280±160) S/m.

The electrical response of prepared network to deformation is presented in Fig. 3. The tape type sample from was prepared having dimension (length/width/thickness) 40/10/0.38 mm. The electrical resistance of the sample was measured through the specimen length by two probe method. The change of resistance by compressing the specimen thickness was measured. Loading/unloading cycles were performed with increasing deformation. The data are presented in Figure 3 as a dependence of resistance change on deformation. The resistance of the network increases by compressing with partially irreversible character after unloading.

![Resistance vs Deformation](image)

**Fig.3** The dependence of normalized electrical resistance on deformation of MWNT network during loading/unloading cycles.

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**REFERENCES**


