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Enhancing effect of $KMnO_4$ oxidation of carbon nanotubes network embedded in elastic polyurethane on overall electro-mechanical properties of composite

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ABSTRACT

The effect of functionalization of multiwalled carbon nanotubes using $KMnO_4$ oxidation and oxygen plasma treatment on the electrical resistance of nanotube network/polyurethane composite subjected to elongation has been studied. The layered composite is prepared by taking a non-woven polyurethane filtering membrane which is made by electrospinning, enmeshing it with carbon nanotubes and melding them into one. The testing has shown tenfold composite resistance increase for the composite prepared from $KMnO_4$ oxidized nanotubes in comparison to the network prepared from pristine nanotubes. The evaluated sensitivity of the treated composite in terms of the gauge factor increases linearly with strain from values around five at the start of deformation to nearly 45 at the strain 12%. This is a substantial increase, which put the composite prepared from $KMnO_4$ oxidized nanotubes among ranges the materials and strain gauges with the highest sensitivity of electrical resistance measurement.

1. Introduction

The oxidation of carbon nanotubes (CNTs) became a frequent way to enhance their chemical reactivity and extend application potentiality. Typically, the nanotube wet oxidation by the potassium permanganate ($KMnO_4$) produces carboxylic acid groups (—COOH) on nanotube surface as well as a significant amount of other oxygenated functional groups such as hydroxyl (—OH) and carbonyl (=O) groups [1,2]. The oxidation enhances gas sensing properties of nanotubes toward organic vapors which can be attributed to better affinity of vapors to the oxidized form of nanotubes [3]. Moreover, it was found that the nanotube network made from oxidized nanotubes has more uniform pore structure and dense morphology with lower porosity in comparison with networks formed by pristine nanotubes [4]. The network structure results from fine nanotube aqueous dispersion, and thus deposition of individual nanotubes and/or only small nanotube agglomerates on filtrating membrane since the presence of oxygen-containing groups facilitates the exfoliation of nanotube bundles and increases their dispersion in polar media [1,2,5].

The oxygen plasma treatment of carbon nanotubes preferentially forms hydroxyl and carboxyl groups on the surface of nanotubes, so that nanotubes can provide a strong affinity to liquid molecules and self-disperse into a liquid medium [6–8]. The plasma treatment has the advantage of being non-polluting and the amount of functional groups grafted on the nanotubes surface can be tailored.

The aim of this paper is to study the effect of nanotube oxidation on electromechanical properties of nanotube network/polyurethane composite both in the course of monotonic elongation and when elongating/relaxing cycles are imposed. In this respect, the main achievement is a multiple increase of gauge factor evaluating electromechanical properties of the composite due to $KMnO_4$ oxidation of nanotubes.

2. Experimental

2.1. Materials

Multiwalled carbon nanotubes (MWCNTs) BAYTUBES C70 P produced by chemical vapor deposition were supplied by the Bayer Material Science AG, Germany (C-purity > 95 wt.%, outer mean diameter ~13 nm, inner mean diameter ~4 nm, length >1 μm and declared bulk density of MWCNT of agglomerates of

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micrometric size 45–95 kg/m^3). The oxidized MWCNTs were prepared in a glass reactor with a reflux condenser filled with 250 cm^3 of 0.5 M H_2SO_4, into which 5 g of $KMnO_4$ (potassium permanganate) as oxidizing agent and 2 g of MWCNTs were added. The dispersion was sonicated at 85 °C for 15 h using thermostatic ultrasonic bath (Bandelin electronic DT 103H). The dispersion was filtered and MWCNTs washed with concentrated HCl to remove MnO_2. Besides MWCNT functionalization by the potassium permanganate, the portion of MWCNTs was treated by low temperature oxygen plasma generated in an inductively coupled radio-frequency discharge at 27.12 MHz in a commercially available O_2 gas at the pressure 50 Pa for 10 min.

Nanotubes were used for the preparation of three aqueous pastes: 1.6 g of MWCNTs (either pristine, $KMnO_4$ oxidized or O_2 plasma oxidized) and ~50 ml of deionized water was mixed with a mortar and pestle. The pastes were then diluted in deionized water with sodium dodecyl sulfate (SDS) and 1-pentanol. Consequently, an aqueous solution of NaOH was added to adjust the pH at value of 10. The final nanotube concentration in suspensions was 0.3 wt.%, concentration of SDS and 1-pentanol 0.1 M and 0.14 M, respectively. The suspensions were sonicated in an apparatus from "Dr. Hielscher GmbH" (ultrasonic horn S7, amplitude 88 μm, power density 300 W/cm^2, frequency 24 kHz) for 2 h and with temperature of ca 50 °C.

MWCNT network (buckypaper) (MWCNT-N) was prepared by nanotube dispersion vacuum filtration thought polyurethane (PU) membrane prepared by technology of electrospinning in cooperation with the SPUR Company a.s. (Czech Republic) [9]. The other networks were prepared from treated MWCNTs in the same way as MWCNT-N. These networks are thereinafter denoted MWCNT-$N_{(KMnO4)}$ and MWCNT-$N_{(O2\ plasma)}$.

For an electrospinning process producing PU non-woven filters, the granulated polyurethane elastomer Desmopan DP 2590A supplied by Bayer Material Science was used. Desmopan DP 2590A is a polyester based thermoplastic polyurethane which is produced using monomers 4,4′-Methylenebis(phenyl isocyanate), polyadipate (1,4-butanediol/adipic acid) and 1,4-butanediol as a chain extender. The limited PU properties provided by the manufacture specify density 1210 kg/m^3, melt temperature 210–230 °C, mold temperature 20–40 °C and strain at break 440%.

The polyurethane granules were dissolved in a mixture of dimethyl formamide/methyl isobutyl ketone (Penta Chemikalie, Czech Republic) with volume ratio 3:1. The polymer weight concentration was adjusted to 16% (w/v) and the mixture electric conductivity to 30 μs/cm by adding NaCl in order to optimize the process. The distance of the steel multijet spinning electrode and the steel plate as the collecting electrode of the electrospinning equipment (SPUR a.s., Czech Republic) was 180 mm, Fig. 1. The total number of nozzles was 18, the length of nozzles 30 mm, the distance between nozzles 20 mm, the nozzle internal diameter 1.2 mm and the outer diameter 2.2 mm. The electric voltage was set to 75 kV (Matsusada DC power supply), the temperature 21 ± 2 °C, the relative humidity 35 ± 2.5% and the flow rate of fresh polymeric solution in one nozzle 1.6 μl/min. The final thickness of PU non-woven filters was about 200 μm.

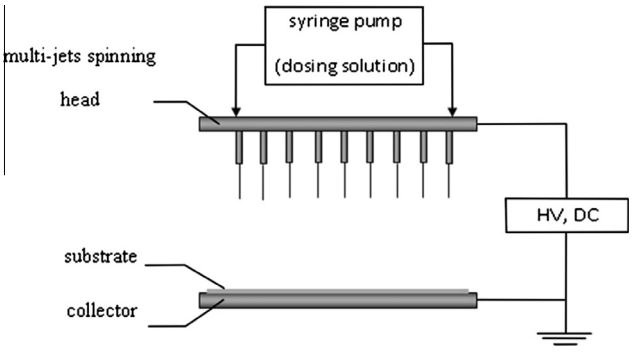

Fig. 1. Schematic diagram of the multijet electrospinning apparatus.

The filtered MWCNT networks were washed several times by deionized water and methanol in situ and dried between two glass microfiber filter papers at 40 °C for 24 h. Polyurethane filter and MWCNT network form the layered structure which was melt welded (at 175 °C) onto the surface of PU tensile test specimen for extension/resistance tests. The partial infiltration of MWCNTs into the filter pores creates an effective interlocking of MWCNT network layer with PU filter which even strengthens when the porous filter is transformed into the polymeric film in the course of compression melt welding.

2.2. Instruments

Pristine, $KMnO_4$, and oxygen plasma-oxidized MWCNTs were analyzed via transmission electron microscopy (TEM) using microscope JEOL JEM 2010 at the accelerating voltage of 160 kV. The sample for TEM was fabricated on 300 mesh copper grid with a carbon film (SPI, USA) from MWCNT dispersion in acetone prepared by ultrasonication, which was deposited on the grid and dried. The structure of MWCNT networks, PU filtering membrane and MWCNT/PU composites were analyzed by scanning electron microscope (SEM) Vega LMU, produced by Tescan Ltd. The samples were deposited on carbon targets and covered with a thin Au/Pd layer. For the observations the regime of secondary electrons was chosen. The content of oxygen in each form of MWCNT networks was detected with help of X-ray spectroscopy (EDX) which is among accessories of SEM microscope. Thermogravimetric analyses (TGA) of MWCNT samples were carried out using thermogravimeter Setaram Setsyt Evolution 1200. The samples were examined under inert atmosphere of helium (5.5 purity, SIAD TP); the gas flow was 30 cm^3/min at the pressure of 101.325 kPa (i.e. 30 sccm) for all experiments. A platinum crucible was used for the sample, the weight of which was about 4 mg. The temperature was increased from ambient up to 1200 °C at the rate of 20 °C/min.

2.3. Measurement of electrical resistance

The purpose of this study is to investigate the change of electrical resistance of different MWCNT network/PU composites in extension. The resistance change of the composite is monitored by a two-point technique by means of Wheatstone bridge (the resistance of the bridge resistors R_1 = 120 Ω, R_3 = 119 Ω, R_2 = 0–1000 Ω and supply voltage 5 V), the multimeter METEX M-3860D and voltage supply METEX AX 502. The time-dependent resistance change of composite was measured by means of the Vernier LabQuest interface system connected to the differential voltage probe and the Wheatstone bridge with sampling frequency 10 and 100 Hz.

For attachment of two copper electrodes to the MWCNT network of the composite samples a screw mechanism was used. The screw tightening was terminated when there was no decrease of network resistance. In that manner, the contact resistance between the network and copper electrodes is controlled and the initial electrical resistance of the system is equally adjusted before the first sample elongation. Initially the network under the screw was pasted by Ag colloid electro-conductive paint Dotite D-550 (SPI Supplies) to decrease the contact resistance. However, the pasting turned out ineffective since no change of the contact resistance was observed. Moreover, the paint crackled and crumbled away in the course of composite elongation.