DEVELOPMENT OF MANUFACTURING PROCESS OF CONDUCTIVE CARBON NANOTUBE NETWORK/POLYSTYRENE COMPOSITES

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ABSTRACT: The composite consisting of filter-supported entangled multiwall carbon nanotube networks were prepared by filtration of nanotube fluid dispersion through a non-woven flexible polystyrene membrane. The nanotubes infiltrate partly into the membrane pores and couple the membrane and the accumulated filtrate layer. The filter-support increases nanotube network mechanical integrity and eliminates the laborious process of peeling off the nanotube network from the usual micro-porous (polycarbonate, nylon) membrane filter followed by the network impregnation to increase its compactness. The composite with embedded nanotube network is shown to be a conductor whose electrical resistance is sensitive to compressive strain. To model the electrical resistance strain dependence, the statistical approach based on Weibull distribution of resistive nanotube contacts is used.

KEYWORDS: carbon nanotube network, non-woven PS membrane, electric resistance, stress sensor.

INTRODUCTION

Recent technology progress relies heavily on the use of materials that can offer advanced structural and functional capabilities. In this respect, entangled carbon nanotube network structures of buckypaper show a great potential for developing high-performance polymer composite materials. The network can proportionally transfer its unique properties into composites and bring substantial improvements in structural strength, electrical and thermal conductivity, electromagnetic interference shielding and other properties in comparison to polymer composites with carbon nanotube particulate filling [1,2]. However, incorporation of conductive nanotube network into a hosting polymer matrix is a difficult task. Traditionally, the network is fixed by a polymer solution (epoxy or bismaleimide resin, polycarbonate solution) to form polymer composites [3,4].

The abovementioned manufacturing of CNT network based polymer composite is rather laborious and may be circumvent by interlocking porous filtrating membrane with entangled CNT. The novel process consists of using the flexible non-woven polystyrene (PS) filter as supporting and integrating element at which, in our case, the multiwall carbon nanotubes (MWCNT) settle and form a network during MWCNT suspension filtration. The obtained MWCNT/PS composite can be used either without adjustment or hot compressed to increase MWCNT fixing to PS membrane. The repeated layering of MWNT/PS membrane sheets yields bulky forms. The flow processing seems promising for a continuous manufacture of carbon nanotube network/polymer composites since the filter-support ensures itself the composite compactness. The usual peeling off the MWCNT network from the membrane is eliminated as well as the network impregnation by means of polymer solutions to increase its mechanical integrity.

EXPERIMENTAL

The acetylene type MWCNT (diameter 10-30 nm, length 1-10 μm) made by Sun Nanotech Co. Ltd., China, are used for preparation of aqueous paste. The paste is diluted in deionised water with sodium dodecyl sulfate and 1-pentanol and sonicated. For making the entangled MWCNT network on a non-woven PS filtration membrane, the vacuum-filtration method is used. The membrane is prepared by electrospinning from solution. PS is solved in a mixture of methyl isobutyl ketone and dimethyl formamide with the volume ratio 3:1 (PS weight concentration is 15 wt%). The nanofiber layer is made using NanoSpider (Elmarco, s.r.o.) equipped by the steel rotation electrode with needles and the steel cylinder collecting electrode (details in [5]). Then the porous layer is subjected to hot pressing at pressure 0.6 MPa and temperature 80°C.

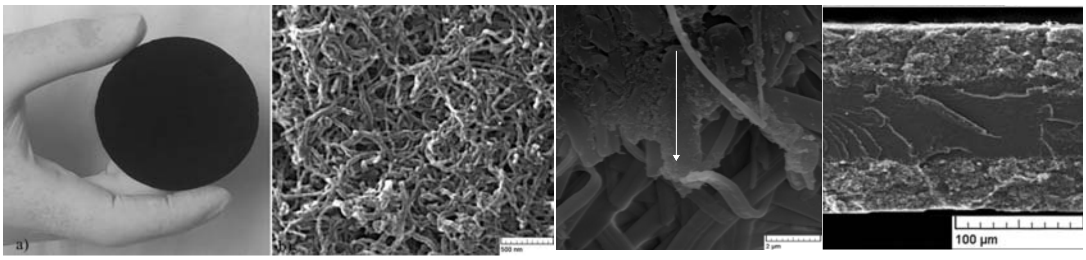
The MWCNT/PS composite is prepared by flow filtration of aqueous MWCNT dispersion through PS filtrating membrane. The start-up phase when the nanotubes are infiltrated in to the PS filter mesh is followed by sedimentation of MWCNT. PS filter-supported filtrate is several times washed by deionized water and methanol in situ. Then the composite is placed between filter papers moisten in acetone and dried between two iron plates at the room temperature for one day. The final drying continued without iron plates at 40 °C throughout another day. The thickness of the non-woven PS filter is typically 0.5 mm and the MWCNT entangled network 0.02-0.4 mm. PS filter-supported MWCNT network composite can be used either without adjustment or the hot compression molding at 190°C converts PS fiber membrane to a film with fixed MWCNT network.

The structure of MWCNT network as well as the cross-section of PS membrane with infiltrated nanotubes and the compressed PS membrane with MWCNT layers was observed by a scanning electron microscope (SEM) made by Vega Easy Probe (Tescan s.r.o., Czech Republic). The sample is deposited onto carbon targets and covered with a thin Au/Pd layer. The observation is carried out in the regime of secondary electrons. The tensile and compression tests are carried out using a simple set-up. The sample stripe (length 45 and width 8 mm) is stepwise extended with 60 sec delay of strain reading in each step. The compressive deformation is adjusted by means of calibrated steel plates and the corresponding resistance along the stripe length is measured by the two-point technique using multimeter Sefram 7338. The loading area between glass plates is 8x8 mm. The electrical contacts are fixed to the stripes by silver colloid electro-conductive paint Dotite D-550 (SPI Supplies).

RESULTS

The structure of entangled MWCNT network of buckypaper and the cross-section of the PS/MWCNT network composite is shown in Fig.1. The MWCNT network is coherent, conductive system (Fig. 1a) which, combined with PS fibrous membrane, increases its rigidity and at the same time keeps its electrical properties. The upper surface of MWCNT network can be seen in SEM micrograph, Fig. 1b. The PS membrane porosity allows infiltrating MWCNT into the membrane during the initial part of filtration till the pores are blocked and pure nanotubes network is formed, Fig. 1c. The arrow in the figure indicates MWCNT infiltration. The composite sheet prepared by double-sided filtration is shown in Fig. 1d. The bulk composite can be prepared by overlaying several PS filter-supported networks and their hardening by hot compression molding.

The results of tensile test are shown in Fig. 2. The initial tensile modulus for MWCNT network is about 600 MPa and the ultimate tensile strength 1 MPa. The test of PS filter-supported MWCNT/PS composite shows a change of mechanical properties in comparison with MWCNT network. The reinforcement increases the tensile modulus to 1300 MPa and the ultimate tensile strength to 10.3 MPa. The corresponding values for tensile modulus and ultimate strength for PS are 1700 MPa and 13.1 MPa, respectively.



(a) (b) (c) (d)

Fig. 1 Free-standing randomly entangled MWCNT network (disk diameter 75 mm, thickness 0.15 mm) (a), SEM image of the surface of entangled MWCNT network (b), SEM micrograph of cross-section of PS fibrous membrane (bottom) with infiltrated MWCNT (c) and the cross-section of compressed composite consisting of PS matrix (middle) and 2 MWCNT network layers (d).

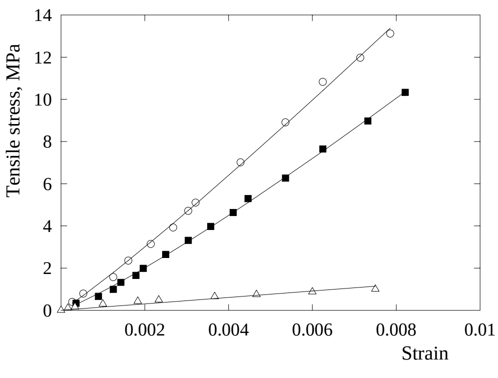


Fig. 2 The comparison of tensile properties of PS filter-supported MWCNT network (squares), MWCNT network (triangles) and PS (circles) in tensile test. The lines represent the power law fitting.

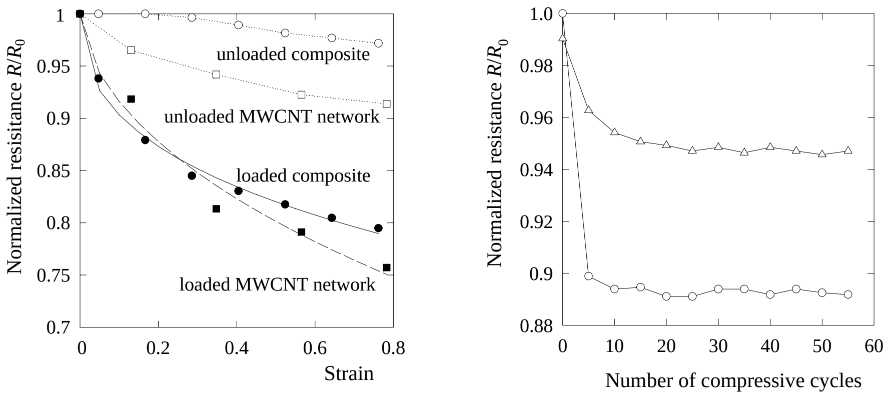


Fig.3 Normalized resistance vs. strain for loaded and unloaded MWCNT/PS composite (circles) and MWCNT network (squares). The solid and dashed stretched exponential line represents Eqn. 2, (left). Normalized resistance vs. number of cycles at the load 3.9 MPa (circles) and 0.4 MPa (triangles) for MWCNT/PS composite (right).

The significant property of new MWCNT/PS composite is its sensitivity to compressive strain. The effect of compression is shown in Fig. 3. The plotted resistance values, R, are normalized with respect to the initial resistance, R_0, recorded at the start of the test. The resistance is measured in each compression step at the preset deformation and for the subsequent unloaded state. The resistance mechanism is apparently not reversible in the initial cycles since there is resistance decrease in off-load state. Nevertheless, the ongoing compression cycles have stabilizing effect on the resistance and after about 20 cycles no resistance change is observed.

Stochastic model of MWCNT network resistance

The electric resistance of the MWCNT network subjected to compressive strain is among others affected by the contact resistance between nanotubes, the nanotube inner resistance mechanism and MWCNT network architecture. Owing to the lack of knowledge of these effects, we translate the results of experimental observation into the probabilistic scheme. Within the framework of this scheme, we assume that the distribution of resistive contact points is such that the joint probability for the total network resistance above a particular level under compressive strain γ is described by the reliability function $S(\gamma)$ for the two-parameter Weibull distribution

$$S(\gamma) = \Pr(\Gamma > \gamma) = 1 - F(\gamma) = \exp\left[-(\gamma/\gamma_0)^m\right] \quad (1)$$

where $F(\gamma) = 1 - \exp\left[-(\gamma/\gamma_0)^m\right]$ is the cumulative distribution function of Weibull distribution. $S(\gamma)$ is a decreasing function, $1 \geq S(\gamma) \geq 0$, and describes the probability of network resistance constancy $\Pr(\gamma)$ under the strain Γ greater than γ (the compressive strain is defined as positive).

The measured dependence of the macroscopic, i.e. network resistance on the compressive strain is in accordance with the chosen probability tendency. Consequently, the following relation of the function $S(\gamma)$ to the normalized network resistance R/R_0,

$$R/R_0 = S(\gamma) = \exp\left[-(\gamma/\gamma_0)^m\right] \quad (2)$$

links appropriately the model prediction with the observed strain dependent network resistance decrease. The reasonably good description of the measured data by the predictive Eqn. 2, shown in Fig. 3 (left) (parameters γ_0=24.9, m=0.41 - solid line, γ_0=6.8, m=0.58 - dashed line), justifies the probability model chosen here for the description of MWCNT/PS composite and MWCNT network resistance change under compression.

FINAL REMARKS

The PS filter-supported entangled multiwall carbon nanotube network composite is a conductive flexible polymeric material. The combined mechanical and electrical properties open new opportunities for the composite use as polymer composite conductors, pressure sensing elements as well as materials for electromagnetic interference shielding and lightning strike protection. A hot press molding process can produce solid bulk composites consisting of multiple-layers of PS filter-supported MWCNT network.

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