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Deformation Theory of an Electro-conductive Composite Composed of Entangled Network of Carbon Nanotubes Embedded in Elastic Polyurethane

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Abstract. A strain sensing polymer composite consisting of a network of entangled multi-walled carbon nanotubes in a thermoplastic polyurethane elastomer is tested by tensile and bending deformation. The composite is prepared by taking a non-woven polyurethane filter membrane, enmeshing it with carbon nanotubes and melding them together. The testing has shown that the material can be elongated as much as 400% during which the electrical resistance is increased more than 270 times. To describe the composite strain dependent resistance, a rheological model is proposed which takes into account a decrease of local contact forces between nanotubes as well as the reduction of number of contacts with deformation. The theory is used for description of sensing element deformation and resistance when simple elongation and repeated bending is exerted.

Keywords: Carbon nanotubes, Entangled network, Mechanical properties, Cyclic deformation.
PACS: 81.05Qk, 81.07De, 83.60Df

INTRODUCTION

The practical use of carbon nanotube (CNT) structures demonstrates their application in the field of sensing technology as novel types of sensors [1]. The interconnected CNT structures are capable of detecting macroscopic electrical resistance change induced by their deformation. The published data show that the electrical response to strain or stress is sufficient and the sensing can be performed in real time [2-4]. Moreover, the deformation process is reversible although some irreversibility is also measured as a hysteresis loop in cyclical loading tests [2,5,6].

The CNT based strain sensitive elements usually consist of a pure CNT entangled network of buckypaper when the resistance response to deformation is governed by nanotube interactions [1,3-8]. The decisive role is played by local resistance in nanotube contacts and the straightening and buckling of nanotubes what affects the number of contacts between nanotubes [5]. Both the tensile [3,5], and compressive

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[1,6,7] deformation of CNT entangled network was tested. In the case of tensile load, CNT network is attached to the surface of monitored tensile specimen by epoxy resin [8], or is encapsulated into the specimen [5].

The change of network electrical resistance may then be detected simultaneously with deformation by a two-point [5], or four-point method [8]. The resistance measured usually does not follow deformation linearly [5], although for small strain (up to ~ 0.02) a linear relationship is found [8]. The evaluative sensing (gauge) factor which measures the network strain sensitivity and is defined as the ratio of the relative resistance change to mechanical strain, reached for encapsulated CNT networks in epoxy resin values comparable with values for metallic strain gauges (0.6 – 2.2) [5]. Significantly higher gauge factor value (7) is shown for a pure single-walled carbon nanotube network [4].

In this paper we study the deformation and electrical resistance change of the polymer composite, which consists of multi-walled carbon nanotube (MWCNT) entangled network of buckypaper embedded in the thermoplastic polyurethane (PU). The composite is prepared by an innovative procedure wherein the non-woven polyurethane filtering membrane and the carbon nanotube filtration cake are integrated by compression molding. The composite can sustain very large deformations, what is promising for its practical use for highly-tensile sensing elements. As an example of how reliable the composite used as a strain sensor is, a human knee flexion and its cyclic movement is tested, that may, for example, be useful in orthopedics and rehabilitation.

EXPERIMENTAL

The details on the preparation of MWCNT entangled network embedded in the thermoplastic polyurethane (MWCNT/PU layered composite) are given in our paper [9]. Purified MWCNTs produced by chemical vapor deposition of acetylene were supplied by Sun Nanotech Co. Ltd., China. The nanotube diameter is 10-30 nm, length 1-10 μm, with a purity of ~90% and (volume) a resistivity of 0.12 Ω.cm. Further details on the nanotubes, obtained by means of the transmission electron microscopy (TEM) analysis, are presented in our paper [6]. The nanotubes were used for the preparation of aqueous paste: 1.6 g of MWCNTs and ~50 ml of deionized water were mixed with a mortar and pestle. The paste was 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 the suspension was 0.3 wt.%, concentration of SDS and 1-pentanol 0.1M and 0.14M, respectively. The suspension was 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 hours and with temperature of ca. 50°C.

The polyurethane non-woven porous membrane for MWCNT dispersion filtration was prepared by electrospinning from polyurethane dimethyl formamide/methyl isobutyl ketone (DMF/MIBK, 1:3) solution. The thermoplastic polyurethane elastomer Desmopan DP 2590A was supplied by Bayer MaterialScience. The ultimate strength of 48.9 MPa, with a strain at break 4.422 and a density of 1.205 $g.cm^{-3}$ were specified by supplier. The adequate PU compression molding temperature was selected to be

175°C, according DSC measurement (Perkin-Elmer Pyris 1) performed at a heating rate of 10°C/min. The conditions of electrospinning were as follows: a PU weight concentration of 16 wt.%, the solution electrical conductivity adjusted to 20 $\mu S.cm^{-1}$ using sodium chloride, an electric voltage of 75 kV (Matsusada DC power supply), a temperature of 20-25°C, and a relative humidity of 25-35%. The membrane was prepared in cooperation with the SPUR, a.s. company of Czech Republic (for a detailed schematic of experimental equipment, see reference [10].

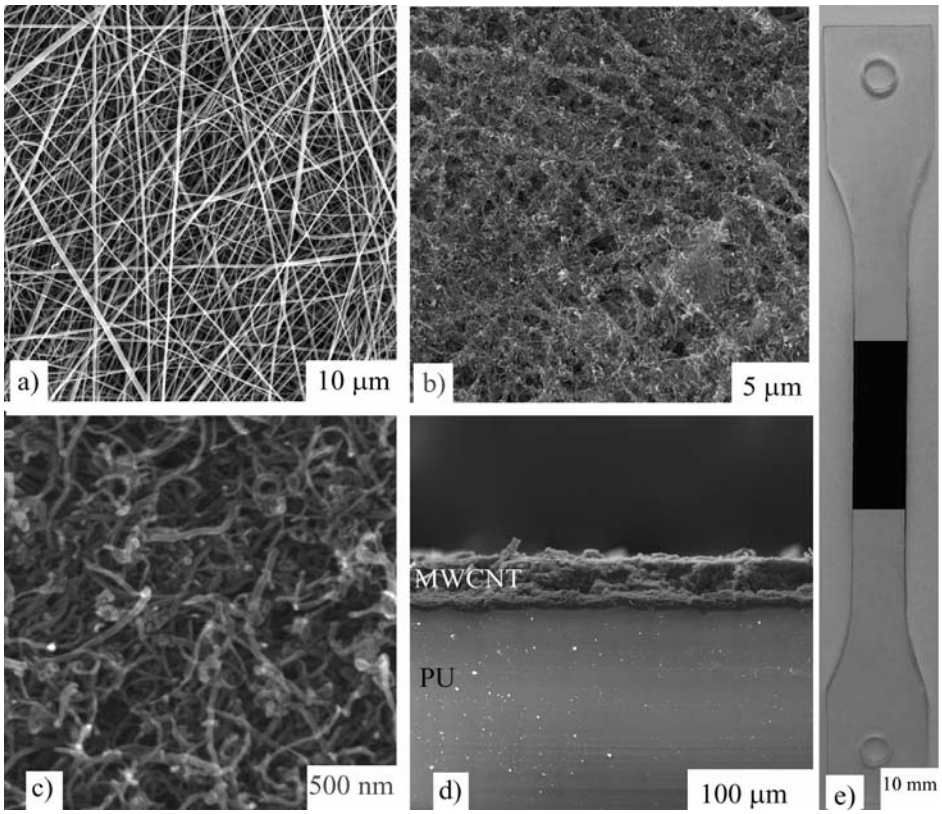

FIGURE 1. a) SEM micrograph of polyurethane non-woven filtering membrane; b) the filtering membrane at the initial stage of filtration process with entrapped nanotubes; c) SEM micrograph of the surface of entangled MWCNT network; d) the composite cross-section after the compression molding; e) photograph of PU dog-bone shaped specimen, for the tensile test, with the fixed stripe of MWCNT/PU composite (black).

For making an entangled MWCNT network, a porous polyurethane membrane and a vacuum filtration method was used. The homogenized dispersion of MWCNTs was vacuum filtered through the membrane. The filtered MWCNT network was washed several times with deionized water and methanol in situ and dried between two glass micro-fiber filter papers at 40°C for 24 hours. SEM micrograph of polyurethane non-woven filtering membrane and a detailed view of the surface of entangled MWCNT network are shown in Figure 1a and c, respectively. The network layer has thickness about 35 μm. Such thin buckypaper is not possible to peel off the filter without damaging it. If some fragments are successfully peeled off the paper they are so brittle that handling them is nearly impossible. However, in our case, both the polyurethane

filter and MWCNT network form the layered structure. 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 molding at 175°C. The initial state of infiltration is shown in Figure 1b. The composite cross-section after the compression molding is shown in Figure 1d. The interaction between MWCNTs and the porous filter is mechanical before the compression molding. Moreover, the melted polymer apparently encloses MWCNTs from MWCNT network surface in the course of molding at 175°C, making firm connection between the polymer and layer of entangled nanoparticles. We presume that this firm connection between layers maintains composite conductance even at extreme elongation and the reversibility of deformation and electrical conductance as well.

MWCNT network/PU composite of the size 10x30 mm can be easily melt welded onto the surface of PU tensile test specimen (dog-bone shaped) for extension and resistance tests, Figure 1e. The shape and dimensions are chosen according to standard EN ISO 3167, with a thickness of 2 mm.

The resistance change of the composite is monitored by a two-point technique under different tensile loading. The experimental set-up is placed into the thermostatic box (Lovibond) and the experimental temperature is set at 25°C. The longitudinal composite resistance is measured 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 5V) and the multimeter METEX M-3860D and voltage supply METEX AX 502. Two electrical Cu contacts are fixed to the MWCNT network by a screw mechanism.

To illustrate the measurement of the resistance of electrically-conductive composite in repeated deformation cycles, the human knee flexion is investigated. The strip of MWCNT network/PU composite is adhered to an elastic knee bandage (83% of polyamide and 17% of elastolan) by means of DMF/MIBK (1:3) solution. The electrical contacts are fixed to the strip by a silver-colloid electro-conductive paint Dotite D-550 (SPI Supplies) and the resistance is measured lengthwise by the two-point technique using multimeter Sefram 7338. The time-dependent resistance change during pedaling on the exercise bicycle is monitored by means of the Vernier LabQuest Interface System connected to the Differential Voltage Probe and the Wheatstone bridge with sampling frequency 100 Hz.

DEFORMATION THEORY

The cross-section of MWCNT/PU layered composite cross-section after the compression molding is shown in Figure 1d [9]. The MWCNT network layer has thickness about 35 μm. The thickness of PU layer is about 1 mm. PU layer is the homogeneous elastic layer supporting nanotube network and preserving its integrity. As far as the description of deformation of PU layer is concerned, the extension and bending of plate may be idealized within the framework of thin plate theory by assuming that deformations are now functions of the two in-plane coordinates (x and y). The x-y coordinate axes are located on the neutral plane of the plate and the z-axis is normal to the x-y plane. The thin plate theory makes two major assumptions: 1) a line normal to the mid-surface of the plate is inextensible (does not stretch), and

2) a straight line originally normal to the undeformed mid-surface neutral plane remains straight and rotates so as to remain straight and normal to the deformed mid-surface plane. These assumptions imply that there is no transverse normal strain (assumption 1) or shear strain (assumption 2). The external loadings generally produce deformations of the plate in the x,y coordinate directions in case of extension and x, y, z coordinate directions in case of bending.

The deformation of very thin layer of MWCNT network is different to deformation of PU layer. The network deformation is induced through the interface formed by the nanotube embedding to the loaded polymer. Consequently, the interface deformation follows the polymer deformation and the nanotube network embedded to polymer preserves the entangled character [9]. However, the deformation of the free MWCNT layer changes uniform network entanglement to non-uniform one which with increasing elongation or bending takes on the form of broken clustered structure [9]. The clustered MWCNT structure does not contribute to the layered composite to withstand the loading and thus only PU layer response to impose deformation. On the other hand, MWCNT layer maintains its electrical conductance even at high extension due to the embedding of nanotubes into the polymer at the interface as well as by the electrical contacts of nanotube clusters secured by long nanotubes [9]. Virtually, the network keeps integrity which can be quantified in terms electrical resistance vs. deformation. About the resistance can be speculated in terms of contacts between entangled nanotubes. When the nanotube network is stretched the nanotubes presumably release from intertubes contacts. The contact release is apparently governed by the competition between the external loading forces transferred from the supporting polymer and frictional intertube forces in the entangled nanotube network. The intertube forces are controlled by the local entanglement of nanotubes which protects the spontaneous release of nanotube contacts by the external force which acts on the nanotubes through interface layer between the polymer and MWCNT network. However, the contact release may also form new intertube contacts. This process of back and force contact reduction and formation under the influence of external forces may be defined by the corresponding transition probabilities per unit time. The generation probability g_n that the network layer being at state n (where n represents altogether the number of intertube contacts), a jump occurs to n+1 and the recombination probability r_n for a jump to n-1.

The variation of acting force on nanotube network yields the distribution of generation probability which approximated by the survival function of well tried Weibull distribution gives, $g_n \propto \exp\left[-\left(\gamma/\gamma_0\right)^m\right]$, where γ is related to applied strain and m and γ_0 are the Weibull shape and the scale parameters, respectively [6]. Consequently, it can be proposed,

$$g_n = g_0 \exp\left[-\left(\gamma/\gamma_0\right)^m\right]\left(N-n\right) = g\left(\gamma\right)\left(N-n\right), \tag{1}$$

where g_0 denotes the generation probability per unit time in the absence of the external force, N the upper bound of states and (N-n) limits the finite range of states n, 0, 1, 2, …, N, and prevents the generation probability from becoming negative.

The intertube contacts may as well appear even under loading though it is relatively insignificant. Thus the recombination probability r_n can be considered indirectly proportional to straining, $r_n \propto n/\gamma$, where n again prevents r_n from becoming negative. On the other hand when the formation of new intertube contacts is significant r_n may increase with flow, $r_n \propto n\gamma$. Generally, the recombination probability is $r_n = r(\gamma)n$.

The stochastic process consisting of the breaking and formation of the intertube contacts runs through the integer states n that represent the number of contacts. The corresponding master equation whose generation and recombination probabilities permit only jump between adjacent states has the form [11],

$$\frac{\mathrm{d}p_n}{\mathrm{d}t} = g_{n-1}p_{n-1} + r_{n+1}p_{n+1} - (g_n + r_n)p_n, \tag{2}$$

where $p_n(t)$ denotes the probability of each state n. The transition probabilities suggested above are linear functions of n but besides that they are also time dependent. Hence it is impossible to give an explicit solution of the master equation other than stationary one. In this respect, the approximation of the transition probabilities by quasi-steady values makes possible to solve the differential-difference master equation in closed-form through the use of a generating function $F(z,t)$ defined for the considered process as,

$$F(z,t) = \sum_{n=0}^{N} z^n p_n(t), \tag{3}$$

where z is an auxiliary variable [11]. Writing Eq. (2) as an equation for $F(z,t)$ after multiplication by z^n and summation over all states n, the solution of that partial differential equation follows from the general solution given in [12],

$$F(z,t) = \left(1 + \frac{r}{g}\right)^{-N} \left\{z + \frac{r}{g} + (1-z)\exp\left[-(g+r)t\right]\right\}^N, \tag{4}$$

as the particular case in which there is initially no released particle.

The first moment of the stochastic variable n corresponds to its average value. Taking derivative of $F(z,t)$ with respect to z and allowing $z \to 1$, the first moment is,

$$n^*(t) = \langle n \rangle_t = \sum_{n=0}^{N} n p_n(t) = \lim_{z \to 1} \frac{\partial(F)}{\partial z}. \tag{5}$$

The evolution of the average number of breaking of intertube contacts up to the maximum number of broken contacts N is then,

$$n^*(t) = N\left\{1 - \exp\left[-(g+r)t\right]\right\}. \tag{6}$$

The electrical resistance of the conducting MWCNT network increases when the strain is applied and breaks intertube contacts. Owing to the complex network arrangement, the correlation between the resistance and its deformation which affects the number of contacts as well as further various quantities is difficult to propose from first principles. However, all states including the final state at $n < N$ correspond proportionally to the resistance change of MWCNT network. Consequently, the first approximation of the relationship between the resistance change and the number of broken intertube contacts may be the following dependence

$$\frac{\Delta R}{R_0} = \frac{N(1+\alpha\varepsilon)}{N-n^*} - 1, \tag{7}$$

where $\Delta R/R_0$ is the relative change of resistance in the network, N and n^* are total number of contacts and the number of broken contacts, respectively.

Owing to the strain ε dependence on time during time dependent deformation, n^* specification can be done in the iterative steps on the assumption that the final number of broken contacts as well as the time dependence of $g(t)+r(t)$ is known. Since it is not this case, generally, it is proceed in the following that the extension or relaxation influence on the MWCNT network resistance is not changing instead of the linear dependence, $\alpha\varepsilon = A$. Then the contact formation rate $r(t)$ is neglected for elongation and $\exp(-r(t)t)$ in Eq. 6 is replaced by $\exp(-at^b)$ with the constant rate of breaking of contacts a. The relaxation period of deformation is then characterized by the neglected rate of intertube contact breaking $g(t)$ and the rate of contact formation is assumed constant, $r = c$. Thus $\exp(-r(t)t)$ is replaced by $\exp(-ct^d)$.

In case of steady resistance-strain dependence, the proposed first approximation (7) must take into account the amount of broken intertube contacts dependent on the strain and not on the time. The evolution of the average number of breaking of intertube contacts is then well described by the Weibull distribution model of intertube contacts [9],

$$n^* = N\left\{1-\exp\left[-\left(\frac{\varepsilon}{\beta}\right)^m\right]\right\}, \tag{8}$$

Then the relative resistance change is

$$\frac{\Delta R}{R_0} = (1+\alpha\varepsilon)\exp\left[-\left(\frac{\varepsilon}{\varepsilon_0}\right)^m\right]^{-1} - 1, \tag{9}$$

where α is a proportionality constant and two Weibull parameters are the shape parameter m and the scale parameter ε_0.

RESULTS

Properties of MWCNT/PU composite consisting of a network of entangled multi-walled carbon nanotubes in thermoplastic polyurethane are tested by tensile and bending deformation. The tensile test shows the conduction limit of the composite during stepwise increase of strain, Figure 2. The data show that the composite is electrically conductive even at the largest strain of 403% when the resistance is more than 47000 Ω ($\Delta R/R_0 = 277$). The resistance increase with strain is continuous without any discontinuity, which is not usual in the case of conductive particulate nano-composites, when an electrical percolation threshold is reached at larger strain. The resistance mechanism is apparently not reversible in the initial cycle since the relaxation curve has a residual resistance increase (1750 Ω; $\Delta R/R_0$ =10.29) in the off-load state. Nevertheless, the ongoing extension cycles have a stabilizing effect on the resistance-elongation loops (see Figure 3). The residual resistance change $(R - R_0)_r$, defined as the residual minimum resistance change during each cycle, tends to reach immediately to an asymptotic value. It indicates that during first deformation the nanotube network gets the structure which stays more or less the same regardless the number of deformation cycles. This mechanical stabilization is favorable for the use of the composite as a sensing element of elongation, especially when the network is suitably deformed in advance.

The mechanism of resistance change during elongation combines possibly a decrease of local contact forces between nanotubes as well as reduction of number of contacts. The decrease of contact forces restrains a contact of nanotubes, which in turn leads to the increase of contact resistance between crossing nanotubes. Besides that the extension straightens the nanotubes what may result in less contacts between them. Since the contact points act as parallel resistors, their decreasing number causes an enhancement of MWNT network resistance.

The quantitative relationship (9) respects the abovementioned mechanism and described thus the experimental results presented in Figure 2 very well. The parameter α , ε_0 and m values are 15.5, 3742, 14.05, respectively.

The result of time dependent deformation testing of MWCNT/PU composite is presented in Figure 3. The testing is equally an example of practical use of MWCNT network/PU composite as a human knee bending is monitored. The measured waveform of resistance change vs. time dependence results form the test performed by the volunteer with the measuring strip of MWCNT network/PU composite on the knee bandage pedaling on an exercise bicycle. The deformation of MWCNT network is apparently tensile in the course of the measurement since MWCNT network bonded to polymer base is on the convex surface of the stripe above its neutral axis. At the same time the regular deformation cycles demonstrate the composite measuring properties under long-lasting cyclic stretching.

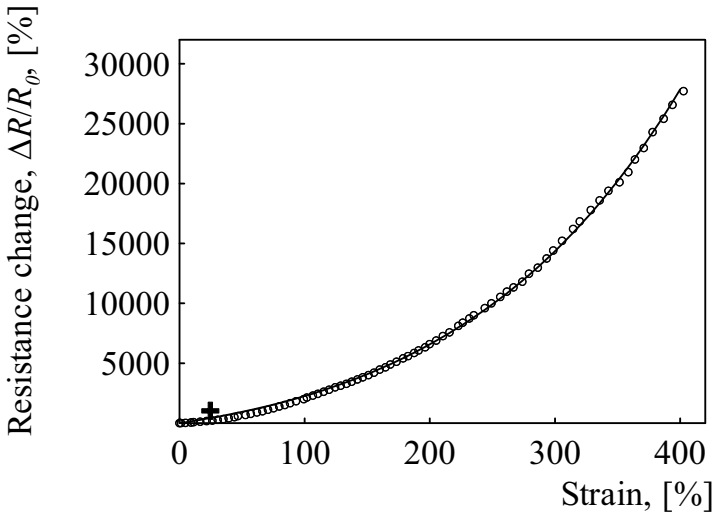

FIGURE 2. Strain dependence of relative resistance change for MWCNT/PU composite. Experimental data are denoted by open circles. The solid line represents description by Eq. 9. The cross denotes the resistance change value in a relaxed state after 403% extension.

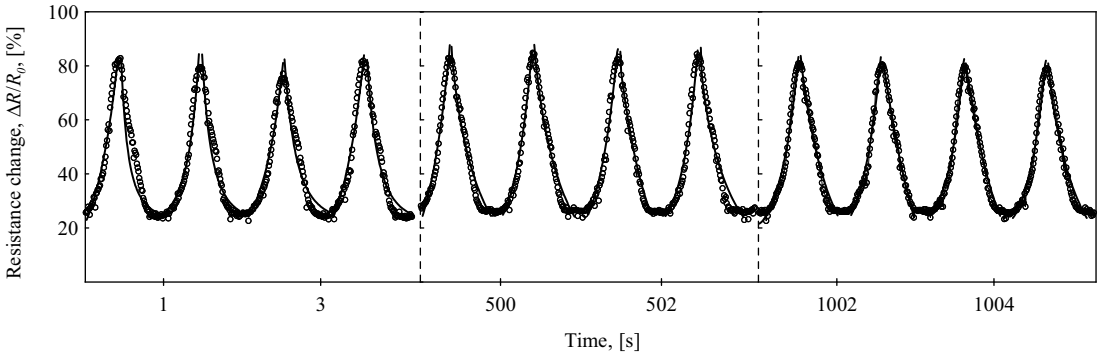

FIGURE 3. The waveform of the normalized resistance during volunteer's cycling on the exercise bicycle scanned by the strip of MWCNT network/PU composite adhered on the knee bandage. The solid line represents description by Eq. 7.

The time dependent resistance change is described by the proposed relationship (7) in both the resistance increasing as well as decreasing part of deformation cycle. The average values of the cycle starting network resistance A and parameters a, b in the up cycle part are 21, 3.7 and 1.2, respectively. The corresponding values A, c, d for down cycle part are 82, -2.9 and 0.8, respectively. The comparison of experimental data and theoretical description provided in Figure 3 shows reasonable correspondence.

CONCLUSIONS

We have introduced a theoretical description of tensile and bending deformation of highly deformable MWCNT network/PU composite composed of the network of electrically-conductive entangled carbon nanotubes embedded in elastic polyurethane. The composite is prepared by taking a non-woven polyurethane filtering membrane, enmeshing it with carbon nanotubes and molding them into one. The testing has

shown the composite can be extended as much as 400 % during which the resistance increases more than 270 times.

The resistance change of MWCNT network/PU composite is considered to correspond to the change of the number of contacts between entangled nanotubes. The description of this resistance change is based on the stochasticity of the breaking and reformation of contacts under the influence of external forces. The stochastic process is defined by the corresponding transition probabilities per unit time. The first approximation of the relationship between the resistance change and the number of broken intertube contacts is then proposed for time dependent resistance change. In case of only strain dependent resistance change, the evolution of the average number of breaking of intertube contacts is then described by the Weibull distribution model of intertube contacts. Both descriptions give a good representation of the experimental resistance change of the composite in the cyclic deformation and simple tensile deformation.

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