Improving sensitivity of the polyurethane/CNT laminate strain sensor by controlled mechanical preload

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Abstract. This article describes strain detection potential of polyurethane/CNT layered composite and further possible enhance of its sensitivity to strain, expressed by value of gauge factor, GF, employing its controlled mechanical preload. In course of its fabrication a non-woven polyurethane membrane made by electro spinning was used as filtering membrane for CNT aqueous dispersion. Final CNT polyurethane laminate composite is prepared by compression molding. Produced polyurethane/CNT composite laminate is electrically conductive and high elastic. Its elongation leads to change of its macroscopic electrical resistance. Changes in resistance are further reversible, reproducible and can monitor deformation in real time. Gauge factor reaches very high values around 8 for strain reaching 3.5 % comparing with conventional metallic strain gauges. Finally, controlled mechanical preload significantly increases value of GF. For example for value of 8.1 % of preload value of GF reaches 23.3 for strain 3.5 %.

1. Introduction
The carbon nanotube networks (CNT-Ns) can proportionally transfer their unique properties into composites and bring about substantial improvements in their properties such as the strength, the electrical and thermal conductivity. For instance, CNT-Ns as a strain sensor has potential advantage in that the networks have high sensitivity to local distributions of stress and strain as well as the ability to sense stresses and strains in different directions in the host materials [1]. In this respect the strain sensitivities of epoxy [1], poly(methylmethacrylate) [2] and thermoplastic polyurethane composites [3] with MWCNT-Ns or SWCNT-Ns have already been studied. Moreover, there are also some studies on the stimulation effect of the functionalization of CNT-Ns with plasma [4,5] as well as the carboxylic acid and amine groups [3] on the electrical properties [4,6] and mechanical properties [4,5] of polyurethane [3,6], polyimide [4] and polycarbonate [5] composites with CNT-Ns.

In this study, the stimulation effect of preloading on the electromechanical properties of thermoplastic polyester-based polyurethane (TPU) laminate with MWCNT-Ns is investigated under elongation and elongation/relaxation cycles and compared with corresponding properties of CNT-N/TPU laminates without preloading.
2. Experimental

MWCNT/Polyurethane laminate tested as a strain sensitive element is a thermoplastics polyurethane (TPU- Desmopan 385S) based composite with layered network made of entangled multi-walled carbon nanotubes of Buckypaper. Sensory layer was made by entangled multi-walled carbon nanotubes (MWCNT-Sun Nanotech Co. Ltd.). PU non-woven filtering membranes were prepared by electrospinning process and aqueous dispersion of MWCNT was vacuum filtration through it. Polyurethane filter with MWCNT network was melt welded (at 175 °C) onto the surface of TPU plate 2 mm thick. MWCNTs were analysed via transmission electron microscopy (TEM) using microscope JEOL JEM 2010 at the accelerating voltage of 160 kV. TPU filtering membrane and MWCNT/PU composites were analysed by scanning electron microscope (SEM) NOVA NanoSEM 450 (FEI). The change of electrical resistance of carbon nanotubes network/polyurethane laminates in extension/relaxation cycles were measured lengthwise by the two-point technique using multimeter Sefram 7338. For attachment of two copper electrodes to the MWCNT network of the composite samples a screw mechanism was used.

3. Results and discussion

The scanning electron microscope (SEM) analysis of mentioned PU non-woven filtering membrane is presented in Fig. 1 a). The transmission electron microscopy (TEM) micrograph in Fig. 1 b) gives a detail view of used nanotubes. Individual nanotubes are entrapped by filtering membrane in the course of MWCNT aqueous dispersion vacuum filtration. The nanotubes infiltrate into membrane pores which are finally blocked by a filtering cake made of pure network of entangled MWCNT [7]. SEM micrograph in Fig. 1 c) shows the upper surface of MWCNT network. MWCNT network is a porous and electrically conductive structure created by entangled nanotubes with electrical conductive junctions between them. The electrical conductivity of the MWCNT network is predominantly determined by the contact resistance in junctions of crossing nanotubes, rather than by resistance of MWCNTs itself. The nanotubes are much shorter than the dimension of straining sample and inter-tube contacts act as parallel resistors between highly conductive MWCNT segments. The final step of the laminate preparation is the melt welding of PU filter and MWCNT resulting about 2 mm thick composite plates. Electromechanical sensitivity of the prepared laminate was tested using dog-bone shape specimens cut out from two-layer laminate, see Fig. 1 d).

Fig. 1 a) SEM micrograph of polyurethane non-woven filtering membrane, b) TEM micrograph of used nanotubes, c) SEM image of the surface of entangled MWCNT network, d) Photograph of PU dog-bone shaped specimen, for the tensile test, with the fixed stripe of MWCNT/PU laminate (black).
The electromechanical behavior of carbon nanotubes network/polyurethane laminates and their preload stimulated form are presented in the following Fig. 2 a-b. The data represents five extension/relaxation cycles (the cycle deformation gradually increases in each 2 minutes cycle up to maximal strain value 3.5 %). The extension/relaxation cycle was five times repeated. The stimulated laminate was prepared by preload elongation 8.1 % lasting 10 minutes. The electromechanical testing was then performed after 20 hours of specimen relaxation. The extension of the each test specimen denoted by black lines, initiates resistance increase (illustrated by red lines). The strain is defined as \( \varepsilon = \frac{\Delta L}{L_0} \), where \( \Delta L \) represents the change in specimen length and \( L_0 \) is the initial length before the first elongation. Resistance changes are defined as the relative resistance change \( R/R_0 = \frac{R-R_0}{R_0} \), where \( R_0 \) is the electrical resistance of the measured sample before the first elongation, and \( R \) is the resistance while elongating. After specimen unloading, deformation of polyurethane specimen decreases what is monitored by the resistance decrease. In the course of strain cycles, some irreversible changes in strain and the relative resistance are observed due to possible residual plastic deformation of TPU and irreversible damage of the electrically conductive MWCNT network. In the second and following cycle series the difference between responses is not such significant comparing with the first cycle series. Similar strain stabilization effect is observed for preloaded specimen when in consecutive cycles the relative resistance change or irreversible part are nearly equal. Moreover, the data in Fig. 2 demonstrates preload stimulation of electro-mechanical sensitivity. For example, the final value at the end of the fifth cycle of the fifth series reaches value of relative resistance change for no preload laminates 25.9 %. On the other hand, the corresponding value at preload 8.1 % achieves the resistance change 72 %.

The data in Fig. 2 reveals also a significant effect of applied preload on the increase of relative resistance change. The change can be successfully quantified by means of a gauge factor (GF), which defines sensitivity of strain gauge as the relative resistance change divided by the applied strain, \( GF = \frac{\Delta R/R_0}{\varepsilon} \). According to calculated GF values presented in Fig. 3, GF for the non-preload laminate is nearly independent on applied strain in the first cycle series since only slowly increases from values of 4.4 to 5.4 is observed. In the following series of cycles GF gradually increases up to values of about 8.2. At the same time, the values are stabilized by the applied strain cycles.

Fig. 2 Response of the relative resistance change, \( \Delta R/R_0 \), to applied strain, \( \varepsilon \), for MWCNT/PU specimen at different values of preload strain. A) No preload specimen, B) preload 8.1 %. The tensile strain step increases in a five consecutive cycles which are five times repeated. The value of strain steps is denoted by black lines and the relative resistance change by red lines.
At the same time, the values are stabilized by the applied strain cycles. It is partially because of the irreversible resistance increase but this increase can be probably also explained as a mechanical stimulation to increase the resistance in the following series of imposed deformation cycles. A similar phenomenon takes place also when the stimulation by preload deformation 8.1 % was applied and GF reaches values around 23.3, respectively. It was found that preload of laminates to higher values of strain, than is its range in the measurement (up to 3.5 %), stabilizes GF values having only small variation in subsequent deformation cycles.

Fig. 4 Dependence of the gauge factor, GF, determined for MWCNT/PU laminate on applied strain for specimen with different values of preload indicated. Each experiment was performed as the tensile strain step increases measurement five times repeated.

4. Conclusions
Multi-walled carbon nanotubes were used in their pure form to prepare entangled networks as a part of MWCNT/TPU laminates. The laminate is made by taking a non-woven polyurethane filtering membrane and enmeshing it with carbon nanotubes. This innovative procedure eliminates the laborious process that is usually used, i.e. peeling off the nanotube network from the common micro-porous (polycarbonate, nylon) filter followed by the network polymeric impregnation to increase its compactness. Prior to deformation, the laminate was subjected to elongation 8.1 %. The subsequent testing consisted of the measurement of laminate deformation by its electrical resistance change in the course of elongation and elongation/relaxation cycles. The results show that the laminate after preloading has an enhanced electrical resistance and increased gauge factor in comparison with the non-preloaded samples.

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