08

The effect of bending on the electrical conductivity of polymer nanocomposite films with single-walled carbon nanotubes

© S.V. Vasin[1], V.A. Sergeev[1,2]

[1] Kotel'nikov Institute of Radio Engineering and Electronics (Ulyanovsk Branch), Russian Academy of Sciences, Ulyanovsk, Russia
[2] Ulyanovsk State Technical University, Ulyanovsk, Russia

E-mail: svasin@ulireran.ru

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The results of an experimental study of the effect of mechanical bending on the conductivity of polymer nanocomposite films of polyvinyl alcohol (PVA) and polymethyl methacrylate (PMMA) with single-walled carbon nanotubes (CNTs) are presented. It is shown that with increasing bending (decreasing the radius of curvature), the resistance of the films increases to 20% of the initial values when the radius of curvature changes to 14 mm. In this case, the dependence of the change in film resistance on bending is not linear. The maximum change in resistance due to bending is observed in nanocomposite films with a CNT mass concentration of 0.5%. The results obtained can be used in the development of bending or strain sensors that can be easily manufactured using available materials, technological methods and equipment.

Keywords: thin films, polymers, flexible sensors, deformations.

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1. Introduction

Currently flexible sensors are the subject of active study and are widely used in many fields, such as medicine, zooculture, robotics, human−machine interface, monitoring of buildings and structures condition etc. The example of such sensors may be temperature sensors, moisture sensors [1], strain sensors that may detect body motion, tactile sensors that enable monitoring of triaxial movement/handling of objects, and proximity sensors preventing potential collisions of people or robots with unknown obstacles [2]. Traditional sensors that are usually made of metals and semiconductors are well-designed technologically and available in the market. However, such sensors usually have the limited range of permissible deformations, which limits their practical use, especially in the so called wearable technology. The promising alternative to such sensors may be the flexible sensors created on the basis of polymer composites with carbon nanotubes (CNT) [3,4].

It is known that the properties of such nanocomposites are determined both by CNT properties and the nature of their distribution and orientation in polymer matrix, however, the relation of nanocomposite properties with the specified CNT properties remains understudied. In its turn, the selection of the polymer matrix material with the required mechanical properties is also critical, so that the material may withstand multiple cycles of various deformation actions in process of operation [5].

This paper studied the effect of bending at electric conductivity of PVA- and PMMA-based polymer composite films with inclusion of CNT.

2. Experiment

Single-wall CNTs of trademark Tuball^{TM} were used. CNT diameter, according to the manufacturer's data, is 1.6 ± 0.4 nm, with length of $\geq 5\,\mu$m. Tubes were cleaned from metal admixtures using their treatment in 2M-solution of hydrochloric acid (HCl) at temperature 80°C for 24 h. To functionalize CNTs with inoculation of polar carboxyl groups (COOH), the tubes were treated in the mixture of concentrated sulfuric (H_2SO_4) and nitric (HNO_3) acids at the volume ratio of (3 : 1) with constant stirring at 90°C for 70 min.

PVA-based composite films were produced from PVA aqueous solution [6]. CNTs were dispersed in deionized water at the required ratio by ultrasonic mixing (ultrasonic disperser UZD2-0,1/22, frequency 22 kHz). To improve compatibility of CNT with the polymer matrix, additional non-covalent functionalization was applied: prior to dispersion of CNTs, 0.1% sodium dodecyl sulfate was added into water. Then both solutions were mixed in a proportion required to obtain the specified concentration of CNTs from PVA mass, mixed using a magnetic mixer for 30 min and cooled down. The required quantity of the solution was poured into Petri dishes and dried at room temperature for 48 h.

PMMA-based composite films were obtained from PMMA solution in toluene with concentrations 0.1−0.25 g/ml [7]. CNT suspensions were prepared by ultrasonic mixing in tetrachloromethane. To obtain specimens with various content of CNTs, the necessary volumes of CNT suspension in tetrachloromethane were added to the PMMA solutions, and mechanical mixing was applied for 2 min. The necessary quantity of the solution was also poured into Petri dishes and maintained at room temperature until complete evaporation of dissolvent (usually not more than 1 h).

From the films obtained, the specimens were cut with size of 3×1 cm, on the edges of which the aluminum contacts were applied by method of thermal evaporation in vacuum to measure conductivity of films with direct and alternating (in frequency range 20 Hz–15 MHz) electric signal. To measure conductivity on DC, programmable power supply source APS-7313 (Aktakom) and picoamperemeter A2-4 (MNIPI) (maximum measurement error 0.5%) were used. Measurement of conductivity on alternating signal was carried out with the help of meters E7-20 (MNIPI) and E7-29 (MNIPI) (basic error 0.2%).

For bend with radius of specified curvature, the specimens of film structures were fixed between two stands on a flexible metal base using a double-sided adhesive tape 3M 4905 with thickness of 0.5 mm. One of the stands was displaced using a micrometer screw with minimum increment 0.1 mm, compressing and bending the base together with the specimen placed thereon. The specimen curvature in its center is an unambiguous function of the distance between its ends [8].

3. Results

Figure 1 shows dependences of change in the resistance of PVA/CNT nanocomposite specimens with various concentration of CNTs on displacement of the specimen end (bend). Maximum sensitivity to bending is demonstrated by films with 0.5% content of CNTs. Conductivity decreases (resistance increases) with the increased bending of the specimen (decrease of the curvature radius) by the value

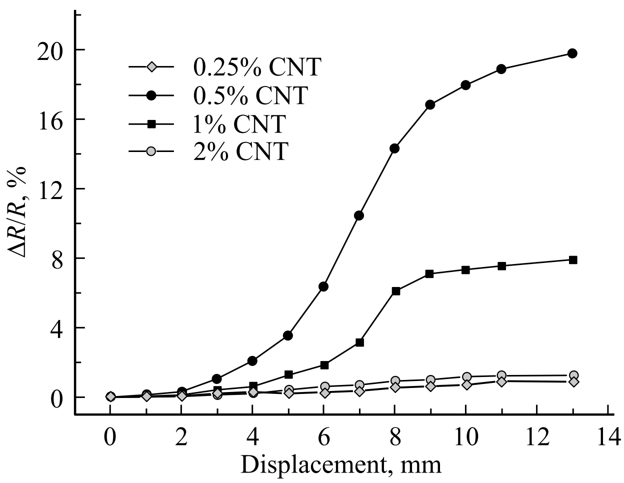

Figure 1. Dependence of change in resistance of PVA/CNT films on DC on displacement of specimen end (resistance values before bending: 0.25% — 162 MΩ, 0.5% — 18.5 MΩ, 1% — 360 kΩ, 2% — 45 kΩ).

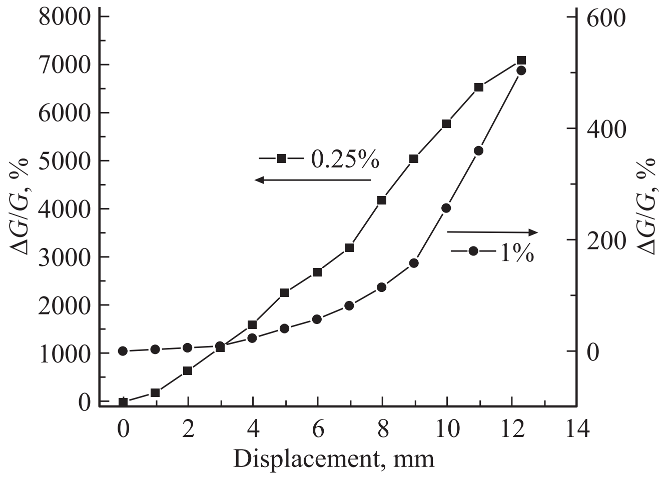

Figure 2. Dependence of PMMA/CNT film conductivity change at frequency of 50 kHz on displacement of the specimen end (conductivity values before bending: 0.25% — $9.4 \cdot 10^{-10}$ S, 1% — $6.3 \cdot 10^{-7}$ S).

up to 20% from the initial one up to the value of the curvature radius 14 mm, corresponding to the displacement of the free specimen end by 13 mm. At the same time one can see that the dependence of the change in the film resistance on bending is not linear. Films with CNT concentration 0.25, 1 and 2% have much lower sensitivity to bending. It should be noted that despite practically twice lower sensitivity to bending in the specimens with CNT concentration 1%, at such concentration the absolute value of resistance is 2 orders higher than the resistance of the specimens with CNT concentration 0.5% ($\sim 10^5\,\Omega$ vs. $\sim 10^7\,\Omega$). This makes it possible to measure current in more „comfortable“ ranges, with the lower level of noise and interference.

When using PMMA/CNT combination, the qualitative appearance of dependences measured on DC is similar to PVA/CNT composite. The main difference consists in a more complicated procedure of CNT dispersion into a PMMA matrix and higher inclination of CNTs to forming agglomerations in a PMMA solution, which complicates production of specimens with relatively high concentration of evenly distributed CNTs.

Dependence of DC conductivity bending sensitivity on CNT concentration seems to be provided for by leap mechanism of current transfer. At high concentrations the average distance between adjacent CNTs is small or absent, and matrix deformation introduced by bending has practically no effect on the formed percolation chains of current transfer. In case of low CNT concentrations the change of the distance between adjacent CNTs introduced by matrix deformation is considerably lower than the initial distance and hardly affects the tunnel current.

Figure 2 presents absolute change of PMMA/CNT film conductivity measured at frequency of test signal 50 kHz depending on the specimen bend. One can see that when

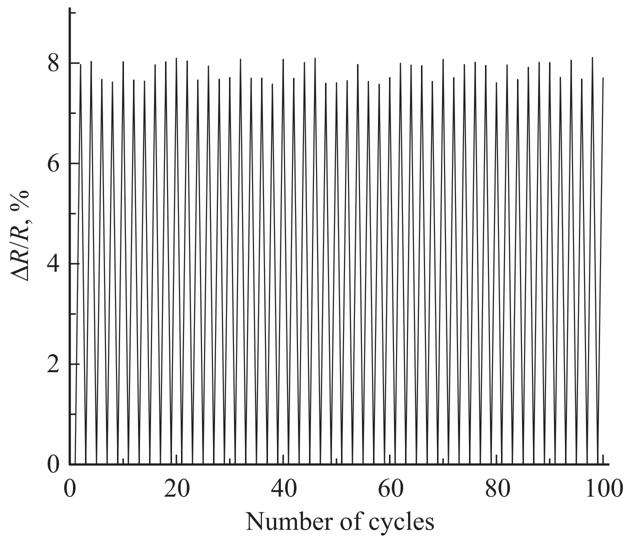

Figure 3. Dependence of change in resistance of PVA/CNT films with CNT concentration 1% on DC on the number of bending–straightening cycles of the specimen to radius of 14 mm.

measuring on alternating signal, the conductivity under specimen bending varies by more than 3 orders, besides, for the smaller CNT concentration this change is substantially greater. However, in this case the main factors influencing the obtained result are the geometric parameters of the specimen (and their change in process of bending), and the measuring signal frequency.

Figure 3 shows as an example the results of the change in resistance of a PVA/CNT specimen with CNT concentration 1% at multiple bending–straightening cycles. The spread of the measured resistance at the same time is within 5%. Similar behavior is specific for PMMA/CNT films, which indicates good mechanical properties of both polymers.

4. Conclusion

The experimental study of effect of mechanical bending on conductivity of polymer nanocomposite PVA and PMMA films with addition of CNTs demonstrated that the increase in bending (decrease in curvature radius) leads to increase of film resistance by value of up to 20% of the initial one up to the curvature radius value of 14 mm. At the same time the dependence of the change in the film resistance on bending is not linear. Maximum sensitivity to bending is observed in specimens with CNT concentration 0.5%.

When measuring on alternating signal, the change in conductivity under specimen bending may achieve 3 and more orders, besides, for the smaller CNT concentration this change is substantially greater. However, in this case the main factors influencing the obtained result are the geometric parameters of the specimen (and their change in process of bending), and the measuring signal frequency.

The study of conductivity under multiple bending–straightening cycles demonstrated good stability and reproducibility of the results from using both PVA and PMMA as a polymer matrix.

The produced results may be used to design bending or deformation sensors characterized by simple manufacturing with application of available materials, technological methods and equipment.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] V.A. Sergeev, S.V. Vasin, M.S. Efimov. Radioelectron. Nanosyst. Inf. Technol. **15**, *1*, 13 (2023).

[2] T. Dong, Y. Gu, T. Liu, M. Pecht. Sensors. Actuators A Phys. **326**, 112720 (2021).

[3] T. Yan, Y. Wu, W. Yi, Z. Pan. Sensors. Actuators A Phys. **327**, 112755 (2021).

[4] F. Khan, T. Mubashir, K. Ahmed, A. Mateen, S. Lee, T. Ahmed. Trans. Electr. Electron. Mater. **24**, *6*, 518 (2023).

[5] X. Wang, W. Guo, Y. Zhu, X. Liang, F. Wang, P. Peng. Appl. Sci. **8**, *11*, 2101 (2018).

[6] S.V. Vasin, M.S. Efimov, V.A. Sergeev. Tech. Phys. Lett. **46**, *6*, 595 (2020).

[7] M.V. Buzaeva, S.V. Vasin, A.M. Nizametdinov, V.A. Sergeev. Nanoelektronika, nanofotonika i nelineynaya fizika: Doklady XVI Vserossiyskoy konferentsii molodykh uchenykh. Saratov (2021). S. 14. (in Russian).

[8] S.V. Vasin, O.V. Ivanov. Avtomatizatsiya protsessov upravleniya **1**, *47*, 101 (2017). (in Russian).

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