

Studying the Mechanical Properties and Structure of the Silver–Polyethylene Terephthalate Composite

D. V. Panov^{a,b}

^a National Research University “Higher School of Economics,” Moscow, 101000 Russia

^b Federal Research Center “Crystallography and Photonics,” Russian Academy of Sciences, Moscow, 119333 Russia

e-mail: dggamer@mail.ru

Received January 12, 2023; revised January 30, 2023; accepted January 31, 2023

Abstract—Silver–polymer composite samples were obtained by the matrix synthesis method. The matrix was polyethylene terephthalate track membranes with pores of different diameters and concentrations. The matrix pores were filled by electrochemical deposition. The structure and mechanical properties of the composite, which consisted of the porous polymer matrix and silver nano- and microwires deposited into pores, were studied. The mechanical properties were determined experimentally by stretching the samples and building the stress–strain diagrams. The length and concentration of nano- and microwires filling the pores of the polyethylene terephthalate matrix were determined by scanning electron microscopy. The nano- and microwire lengths in the same sample are not equal; frequent crossings of the wires were also observed. The crossing probability and the number of nano- and microwire crossings were calculated using a previously developed procedure based on the single bond method. It was shown that the mechanical properties of the metal–polymer composite are significantly affected by the number of wire crossings and, at the same concentration of wires, by the wire diameter.

Keywords: matrix synthesis, track membranes, electrochemical deposition, nano- and microwires, mechanical properties

DOI: 10.1134/S2075113323050337

INTRODUCTION

Currently, flexible electronics is intensely developed and the demand for sensors and various active elements is persistent. A decrease in the size of elements makes the use of nano- and microstructures and study of their structural features and properties relevant and topical [1–3]. In addition, these structures exhibit unique and promising properties that significantly distinguish them from bulk materials [4].

The advances in this field gave a boost to the creation of composites based on one-dimensional nanostructures with special properties. Such structures include nanowires and their arrays [5, 6]. One of the most common ways of their production is the matrix synthesis method, which consists in filling through pores of regular shape with a required substance in a specially fabricated porous matrix [7, 8]. The matrices are conventionally porous structures, e.g., porous alumina, polymer track membranes, etc. [9–12].

In this work, polyethylene terephthalate (PET) track membranes were used, which had the strict geometry of pores and their random arrangement. Track membranes are created by exposure of a polymer matrix to high-energy heavy ions. In this case, the

irradiation conditions prevent the formation of through pores strictly perpendicular to the surface; therefore, they inevitably cross. Polymer track membranes are flexible and allow one to control the pore shape. In track membranes, the pore concentration and diameter can be varied independently over wide ranges [13].

The advantage of the silver–polymer composite is the possibility of its use in aggressive environments due to the chemical inertness of silver and PET; in addition, nano- and microwires of this composite can be used as components of flexible electronics, photovoltaic converters, flexible heaters, etc.

The aim of this work was to study the structure and mechanical properties of the composite samples consisting of a PET polymer matrix and silver nano- and microwires deposited into its pores.

EXPERIMENTAL

The matrix synthesis of nanostructures can be divided into several stages (Figs. 1a–1d): selection of a suitable matrix, formation of a conducting layer, and electrochemical filling of matrix pores with a desired material.

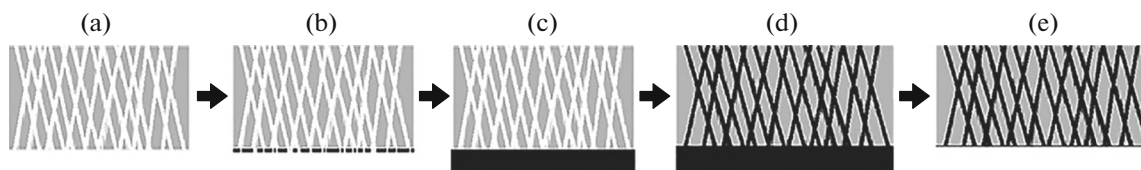


Fig. 1. Stages of the composite sample preparation: (a) selection of a porous matrix, (b) formation of a conducting layer, (c) strengthening of the conducting layer, (d) electrochemical deposition of silver into pores, and (e) selective removal of the conducting layer.

Figure 1 illustrates the stages of preparation of a composite sample based on porous PET with silver nano- and microwires deposited into the matrix pores.

At the first stage (Fig. 1a), the matrix was chosen to be made of three types of 12- μm -thick porous PET films with pore diameters of 100, 400, and 600 nm and a pore concentration of 1.2×10^9 , 6.3×10^7 , and $3.9 \times 10^7 \text{ cm}^{-2}$, respectively (Joint Institute for Nuclear Research, Dubna, Moscow oblast, Russia; the pore concentrations were set by the manufacturer).

At the next stage, a conducting layer was formed on the matrix surface. A thin copper layer was deposited onto the matrix surface by thermal sputtering on a VUP-4 device (Fig. 1b). The thickness of the layer deposited onto the sample was calculated as

$$h = \frac{m}{4\pi R^2 \rho}, \quad (1)$$

where m is the weight of the sputtered material, R is the distance from the heating coil to the sample, and ρ is the density of the sputtered material.

The distance from the heating coil to the sample was 6 cm, and the sample weight was 400 mg. As a result, the calculated thickness of the deposited layer was $\sim 100 \text{ nm}$.

Next, the obtained thin layer was built up by depositing an additional thick copper layer over the previous one (Fig. 1c). This layer was necessary to increase the electrical conductivity. The build-up was carried out by copper deposition in a galvanic bath using an electrolyte containing 200 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 16 g/L H_2SO_4 . The galvanostatic deposition was performed with an Ellins P-2X potentiostat–galvanostat at a potential of 0.6 V. The weight of the resulting layer was calculated according to the Faraday law

$$m = \frac{q}{F} \frac{M}{z} = \frac{\bar{I}t}{F} \frac{M}{z}, \quad (2)$$

where q is the total electric charge passed through the substance, F is the Faraday constant, M is the molar weight of the substance, z is the valence, \bar{I} is the average current, and t is time.

Knowing the weight, we can calculate the thickness of the galvanically deposited contact layer as

$$H = \frac{m}{\rho S}, \quad (3)$$

where S is the sample area and ρ is the copper density.

The calculated layer thickness was $\sim 5 \mu\text{m}$.

After that, silver was deposited electrochemically into pores of the selected matrices (Fig. 1d). The electrolyte comprised AgNO_3 (30 g/L), $\text{K}_4[\text{Fe}(\text{CN})_6]$ (50 g/L), K_2CO_3 (40 g/L), and KSCN (100 g/L). The deposition was performed in the potentiostatic mode at a potential of 0.9 V until pores were completely filled with the metal. The matrix surface area was 12 cm^2 . A silver anode was used.

At the last stage, to obtain the metal–polymer composite, the copper contact layer was selectively removed using a H_2O_2 solution supplemented with $\text{C}_6\text{H}_8\text{O}_7$ (300 g/L) and NaCl (50 g/L) (Fig. 1e).

In the course of the study, the synthesized samples were investigated by scanning electron microscopy (SEM) with a JEOL JCM-6000 Plus electron microscope in the secondary electron mode at an accelerating voltage of 15 kV. The wire composition was determined by energy dispersive X-ray spectroscopy (EDX).

The mechanical properties of the samples were determined experimentally in the uniaxial tension mode at a speed of 2 mm/min on a Shimadzu Autograph AGS-5kN universal testing machine equipped with the software for their automatic calculation. Strip specimens with gauge dimensions of $5 \times 18 \text{ mm}$ were cut out from the composite samples with a REY RAN manual punching press. The stretching direction was chosen to be parallel to the projection of the axis of a cylindrical pore onto the film surface.

RESULTS AND DISCUSSION

The obtained metal–polymer composites had pore diameters of 100, 400, and 600 nm at pore concentrations of 1.2×10^9 , 6.3×10^7 , and $3.9 \times 10^7 \text{ cm}^{-2}$, respectively. The polymer film thickness was $12 \mu\text{m}$. Nano- and microwires were grown until pores were completely filled. The resulting composites were investigated by the SEM and EDX methods.

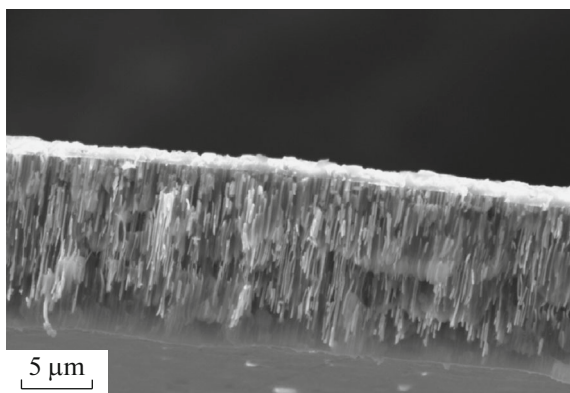


Fig. 2. Cross-sectional SEM image of the PET-based composite with silver nanowires 100 nm in diameter.

Figure 2 shows a cross-sectional SEM image of the matrix with silver nanowires. It can be seen that they are not strictly perpendicular to the matrix surface. The lengths of nano- and microwires filling the PET matrix pores in the same sample are not equal, and numerous wire crossings are frequently observed. The electron microscopy study was carried out using EDX. Figure 3 presents the EDX spectrum of the composite.

It can be concluded from the EDX data (Fig. 3) that the main chemical elements in the composite are carbon, oxygen, and silver (carbon and oxygen are contained in PET; hydrogen peaks are not detected). Table 1 presents the exact chemical composition of the synthesized material.

Next, the specimens of the composite samples were subjected to tensile testing. Figure 4 shows the stress–strain diagrams of the specimens during the tensile testing.

The mechanical properties of the composite samples were examined on strip specimens 1–6 with pore diameters of (1, 2) 100, (3, 4) 400, and (5, 6) 600 nm and respective concentrations of 1.2×10^9 , 6.3×10^7 , and $3.9 \times 10^7 \text{ cm}^{-2}$. Specimens 1, 3, and 5 were cut from the central area of the matrix; and specimens 2, 4, and 6, from the edge of the matrix. Table 2 lists the mechanical properties of the examined specimens.

The difference between the mechanical properties (first of all, plasticity) of specimens 1 and 2, which had the same nanowire diameter, but were cut from different (central and peripheral) parts of the composite sample, is caused by features of the deposition and, consequently, by the difference in the geometric parameters. The fact is that the difference between the properties of different (central and peripheral) parts of the nano- and microwire array (the metal–polymer composite) is related to the difference between the ion concentrations in these parts, near the matrix surface. Due to the natural convection of the electrolyte and the edge effect of the galvanic cell, the concentration of deposited silver ions is higher at the edges of the

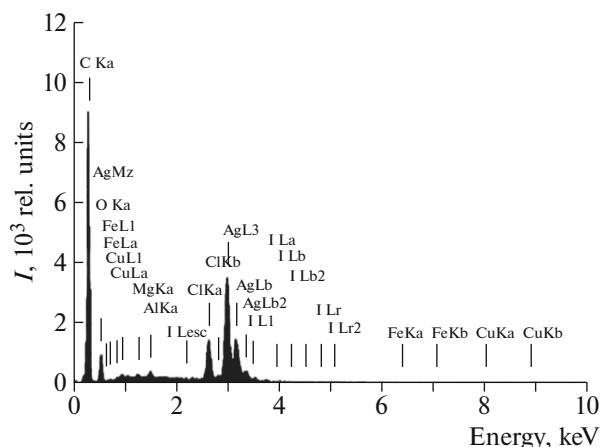


Fig. 3. Energy-dispersive spectrum of the composite with nanowires 100 nm in diameter.

deposited area than in the central part; i.e., there is the so-called growth gradient during electrochemical deposition of the material [14, 15]. Since the ion concentrations and ion current densities are high, the nanowire growth rate on the periphery of the composite is also higher, which induces additional stresses in the structure of the peripheral wires and, consequently, leads to a lower plasticity of the peripheral part of the composite as compared with the central one.

It is noteworthy that pores were filled until the appearance of the so-called overgrowths (the areas where the deposited metal went beyond the matrix), which is undesirable (Fig. 5).

A similar situation was observed when comparing specimens 3 and 4 and specimens 5 and 6.

When comparing the composites with different pore diameters, but approximately equal pore concentrations, it is necessary to take into account the chains of crossing nano- and microwires. The fact is that, when filling the pores inclined to the matrix surface,

Table 1. Chemical composition and element contents in the silver–PET composite

Chemical element	Content	
	wt %	at %
C	45.66	68.32
O	21.94	24.64
Mg	0.07	0.05
Al	0.3	0.2
Cl	3.44	1.74
Cu	2.38	0.67
Ag	26.21	4.37
I	0	0

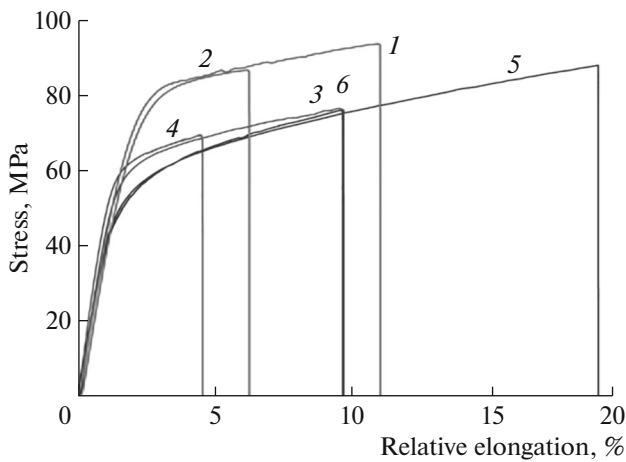


Fig. 4. Stress–strain diagrams of specimens of the silver–PET composite with pore diameters of (1, 2) 100, (3, 4) 400, and (5, 6) 600 nm. Specimens 1, 3, and 5 were cut from the central part of the matrix surface; and specimens 2, 4, and 6, from the edge of the matrix.

arrays of mutual pore crossings can be formed (Fig. 2). These arrays form a network of crossing nano- and microwires in the composite, which can be a strengthening factor. Similar results were reported by Doludenko et al. [16].

In this study, the probability of crossing of nano- and microwires was calculated according to a published procedure [16, 17].

In the investigated metal–polymer composite, the probability of crossing of wires in the specimens cut from the central part of the composite surface was calculated according to the procedure proposed by Doludenko et al. [16] as

$$P_{\text{cross},i} = \frac{V_{30}}{V_m} \cdot i! \times \left(1.8 \frac{V_{-30}}{V_m} \frac{V_{\text{ind}}}{V_{\text{nanowires}} - V_{\text{ind}}} \frac{\sqrt{l^2 - H_f^2}}{\bar{r}H} \right)^{i-1}, \quad (4)$$

where $P_{\text{cross},i}$ is the probability of crossing of the wires grown in the track membrane; V_{30} and V_{-30} are the vol-

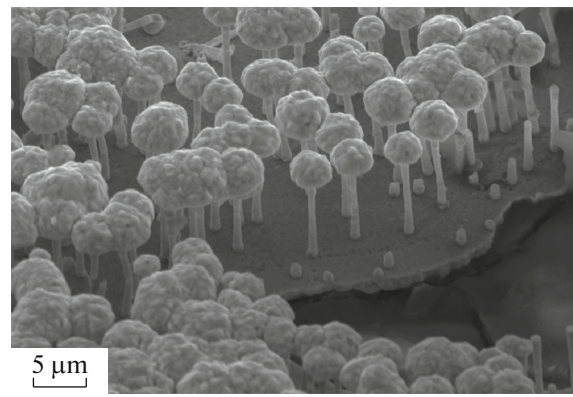


Fig. 5. SEM image of the nanowires with overgrowths.

umes occupied by pores with angles of inclination to the surface plane of 0° – 30° and -30° – 0° , respectively; V_m is the matrix volume; $V_{\text{nanowires}} = 2\pi\left(\frac{d}{2}\right)^2 H_f$ is the volume of a wire; l is the average wire length; H_f is the wire length; and $\bar{r}H$ is the minimum distance between pores in the horizontal projection, related to the features of the track membranes used, which have an angle of inclination of no more than $\pm 0.5^\circ$ to one of the directions (this definition of $\bar{r}H$ was borrowed from Doludenko et al. work [16], where calculations were made using Eq. (4)).

The number of pore crossings in the matrix is

$$N_{\text{cross},i} = P_{\text{cross},i} N, \quad (5)$$

where N is the pore concentration, cm^{-2} .

Table 3 presents the results of the calculation.

Specimens 1, 2, and 3 differ in nano- and microwire diameters and pore concentrations.

Note that, in the calculation, the crossings were taken into account only for the nano- and microwires for which the crossing with other wires occurred in the volume V_{10} that was no less than 10% of the total volume.

Table 2. Mechanical properties of the silver–PET composite specimens

No. of specimen	Offset yield strength, $\sigma_{0.2}$, MPa	Ultimate strength, σ_U , MPa	Relative elongation, %
1	70.03	95.34	11.39
2	69.96	88.22	6.47
3	52.64	77.98	9.96
4	52.60	70.83	4.66
5	41.33	89.57	19.73
6	41.24	65.32	4.71

Table 3. Calculated numbers of pore crossings in the matrices

Property	Specimen 1	Specimen 2	Specimen 3
Nano- and microwire diameter, d , nm	100	400	600
Pore concentration, N , cm^{-2}	1.2×10^9	6.3×10^7	3.9×10^7
Calculated number of crossings $N_{\text{cross},i}$	3.15×10^5	3.44×10^4	4.81×10^4

The wire volume V_{ind} in V_{10} was determined from the formula

$$V_{\text{ind}} = \pi \left(\frac{d}{2} \right)^2 d, \quad (6)$$

where d is the pore diameter.

A significant difference between the calculated numbers of crossings of the studied wires 100, 400, and 600 nm in diameter in the corresponding specimens is due to the significant difference in the pore concentration in the track membranes used.

Thus, based on the data obtained by testing the mechanical properties of the metal–polymer composite, it can be concluded that the crossing of the wires is indeed a factor strengthening the investigated nanocomposites. Note that, to correctly compare the wires of different diameters, the specimens cut from the central part of the composite surface were used.

Table 3 shows that the number of wire crossings is the largest in the composite with a wire diameter of 100 nm and the highest wire concentration; according to Table 2, it has the highest ultimate strength.

For specimens 3 and 5 with wire diameters of 400 and 600 nm, respectively, which have the pore concentrations and numbers of crossings of the same order, the relative elongations of the former is half as large as that of the latter; i.e., the specimens with a large wire diameter are much more plastic. Such a difference in the plasticity of the specimens is probably due to a larger amount of silver in specimen 5 as compared with specimen 3.

CONCLUSIONS

The structure and tensile strength properties of the silver–polymer composite were studied.

It was found that the lengths of nano- and microwires filling pores of the PET matrix in the same sample are not equal, and there are numerous mutual crossings of the wires.

The probabilities of the nano- and microwire crossings were calculated. It was shown that the mechanical properties of the metal–polymer composite are significantly affected by the number of wire crossings and, at the same concentration of wires, by their diameter.

The results obtained can be used to create metal–polymer composites with desired mechanical properties.

ACKNOWLEDGMENTS

The scanning electron microscopy study was carried out on the equipment of the Center for Collective Use, Federal Research Center “Crystallography and Photonics,” Russian Academy of Sciences, Moscow, Russia.

FUNDING

This study was carried out in part within the State Assignment of the Ministry of Science and Higher Education of the Russian Federation for the Federal Research Center “Crystallography and Photonics,” Russian Academy of Sciences, Moscow, Russia.

CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

REFERENCES

1. Eliseev, A.A. and Lukashin, A.V., *Funktsional'nye materialy* (Functional Nanomaterials), Tret'yakov, Yu.D., Ed., Moscow: Fizmatlit, 2010.
2. Anishchik, V.M. et al., *Nanomaterialy i nanotekhnologii* (Nanomaterials and Nanotechnology), Borisenko, V.E. and Tolochko, N.K., Eds., Minsk: Belarus. State Univ., 2008.
3. Borisenko, V.E., Danilyuk, A.L., and Migas, D.B., *Spintronika* (Spintronics), Moscow: Lab. Znaniy, 2017.
4. Martin, C.R., Nanomaterials: A membrane-based synthetic approach, *Science*, 1994, vol. 23, no. 266, pp. 1961–1966.
5. *Electrodeposited Nanowires and Their Applications*, Lupu, N., Ed., IntechOpen, 2010.
6. Pena, D.J. and Mbindyo, J.K.N., Template growth of photoconductive metal–CdSe–metal nanowires, *J. Phys. Chem.*, 2002, vol. 106, pp. 7458–7462.
7. Petukhov, D.I., Napolskii, K.S., and Eliseev, A.A., Permeability of anodic alumina membranes with branched channels, *Nanotechnology*, 2012, vol. 23, p. 335601.
8. Masuda, H. and Fukuda, K., Ordered metal nanohole arrays made by a two-step replication of honeycomb structures of anodic alumina, *Science*, 1995, vol. 268, no. 5216, pp. 1466–1468.
9. Proenca, M.P., Sousa, C.T., Ventura, J., Vazquez, M., and Araujo, J.P., Ni growth inside ordered arrays of alumina nanopores: Enhancing the deposition rate, *Electrochim. Acta*, 2012, vol. 72, pp. 215–221.

10. Davydov, A.D. and Volgin, V.M., Template electrodeposition of metals, *Rev. Russ. J. Electrochem.*, 2016, vol. 52, no. 9, pp. 806–831. <https://doi.org/10.1134/S1023193516090020>
11. *Magnetic Nano- and Microwires: Design, Synthesis, Properties and Applications*, Vázquez, M., Ed., Woodhead, 2015.
12. Pullini, D., Influence of deposition potential on structure of ZnO nanowires synthesized in track-etched membranes, *J. Electrochem. Soc.*, 2012, vol. 159, no. 4, pp. 45–52.
13. Mitrofanov, A.V., Apel, P.Yu., Blonskaya, I.V., and Orelovitch, O.L., Diffraction filters based on polyimide and poly(ethylene naphthalate) track membranes, *Tech. Phys.*, 2006, vol. 76, no. 9, pp. 121–127.
14. Volgin, V.M. and Davydov, A.D., Natural-convective instability of electrochemical systems: A review, *Russ. J. Electrochem.*, 2006, vol. 42, pp. 567–608.
15. Kalinin, I.A., Davydov, A.D., Leontiev, A.P., Napol'skii, K.S., Sobolev, A., Shatalov, M., Zinigrad, M., and Bograchev, D., Influence of natural convection on the electrodeposition of copper nanowires in anodic aluminium oxide templates, *Electrochim. Acta*, 2023, vol. 441, p. 141766.
16. Doludenko, I.M., Volchikov, I.S., Turenko, B.A., Koshchelev, I.O., Podkur, P.L., Zagorskiy, D.L., and Kanevskii, V.M., Electrical properties arrays of intersecting of nanowires obtained in the pores of track membranes, *Mater. Chem. Phys.*, 2022, vol. 287, p. 126285.
17. Clark, P.J. and Evans, F.C., Distance to nearest neighbor as a measure of spatial relationships in populations, *Ecology*, 1954, vol. 35, pp. 445–453.

Translated by E. Bondareva

Publisher's Note. Pleiades Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.