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Electrically conductive nanocomposite bituminous binders containing carbon nanotubes and multilayer graphene

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Abstract: In the modern literature, there is practically no data on the electrical characteristics of bituminous binders modified with carbon nanotubes and graphene nanoplates, while they are necessary for the design and development of innovative asphalt pavement compositions, sensitive to the super-high-frequency microwave radiation. Contemporary bituminous binders are multi-component systems, that may contain polymers, rubbers, synthetic or natural resins, inorganic salts, and even fragrances. As a result of the application of modifying additives, bitumen acquires high performance characteristics. A special class of modifiers are micro- and nano-sized electrically conductive fibers and particles (steel wool, carbon fibers, carbon black, carbon nanotubes, graphene nanoplates). The use of which makes it possible to ensure the sensibility of bituminous binders to super-high-frequency microwave radiation and the implementation of the process of healing cracks in an asphalt pavement with its subsequent regeneration. As part of the study, the authors developed an original technique to produce bituminous binders modified with carbon nanotubes and multilayer graphene. Modified bituminous compositions in the concentration range from 0.2 to 6 and from 0.2 to 11 wt. % for multi-walled carbon nanotubes (MWCNT) and multilayer graphene nanoplates (MG), respectively were experimentally obtained. For the first time, the dependence of the specific volume electrical conductivity of bitumen-based nanocomposites on the concentration of nanostructured carbon filler (MWCNT and MG) was researched. The maximum values of electrical conductivity were 4.76×10^{-4} S/cm and 3.5×10^{-4} S/cm for nanocomposites containing 6 wt. % MWCNT and 11 wt. % MG, respectively. The study determined the filler volume fractions at the percolation threshold for nanocomposites containing MWCNT and MG. They amounted to 0.22 and 2.18, respectively. The formation of a percolation contour in nanocomposites containing MWCNT occurs at significantly lower filler concentrations compared to bituminous compositions containing MG.

Keywords: bituminous binders; electrically conductive nanocomposites; carbon nanotubes; multilayer graphene; graphene nanoplates; percolation threshold.

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INTRODUCTION

To meet the high contemporary requirements for the performance characteristics of road surfaces, it is necessary to introduce modifying additives into the composition of bituminous binders, the main of which are polymers and rubbers [1; 2]. The application of modifying additives improves the performance characteristics of bitumen, such as heat, frost resistance, load resistance, elasticity, and durability [1; 2].

Over the last years, due to the intensive development of nanotechnologies, it became possible to consider nanomaterials as modifying additives for bituminous binders used in asphalt pavements [3]. It is proved that the application of modifying additives of nanosilica, nanoclay, and Fe_2O_3 nanoparticles, improves the mechanical characteristics (plastic strain value, elasticity modulus, and tensile strength) of asphalt pavements [4]. However, the high cost of nanomaterials and the short service life of modified asphalt pavements have led to low economic efficiency of the use of nanosilica, nanoclay, and Fe_2O_3 nanoparticles as bituminous binder modifiers [4].

The most promising modifiers for bituminous binders are carbon nanotubes and graphene nanoplates, which have excellent mechanical characteristics [5]. In the work [6], for the samples of asphalt concrete mixture, modified with carbon nanotubes (at a CNT concentration of 1 wt. %), an increase in tensile strength, elastic modulus, and fatigue strength by 17, 55, and 270 %, respectively, was shown. Due to adding graphene nanoplates to the asphalt mix with a concentration of 3 wt. %, the tensile strength of the modified samples increased by 150 % compared to the control one [7].

The effective use of carbon nanomaterials as bituminous binder modifiers allows applying an innovative approach to healing cracks in an asphalt pavement by exposure to microwave radiation followed by regeneration of this pavement [3]. In [8], ordinary bitumen was modified with carbon nanotubes and graphene nanoplates, and the efficiency of microwave radiation absorption in the obtained compositions was studied. The concentrations of MWCNTs (multi-walled carbon nanotubes) and graphene were 10 % of the bitumen volume. The results of the study showed that both additives increase the heating rate of bitumen under the action of microwave radiation, but the heating rate of samples modified with CNTs is 24 % higher than that of bitumen modified with graphene. The authors of [9] analysed the characteristics of microwave heating of an asphalt mix containing graphene nanoplates at a concentration of 1 and 2 wt. %. The study results showed, that the addition of 2 wt. % of graphene to the asphalt mix doubles the sample heating rate and, therefore, increases the energy efficiency of the sample regeneration process under the action of microwave radiation. Similar results were obtained by adding 9 wt. % of slag to the asphalt mix.

The application of MWCNTs, and other microwave-susceptible carbon nanostructures as modifiers, leads to an improvement of the performance properties of bituminous binders at significantly lower concentrations compared to metal fiber [3; 10]. Moreover, metal fiber has a rather high cost, and the selection and manufacture of modified bitumen compositions are complicated by the shape of the filler particles and reduced adhesion of bitumen to stainless steel [3; 10]. Therefore, the use of carbon nanomaterials as modifiers in asphalt mixes will both improve the service characteristics of these mixtures, and intensify the process of heating the road surface with electromagnetic microwaves.

To study the mechanisms occurring under the action of microwave irradiation in nanocomposite bitumen systems containing carbon nanostructures, the information on the electrical characteristics of these systems (specific electrical conductivity, the volume fraction of the filler at the percolation threshold, and the critical electrical conductivity index) is required. Unfortunately, in the contemporary literature, there is only one work on the study of the electrical conductivity of bitumen compositions modified with graphene nanoplates, and the data are given for only two concentrations – 1 and 2 wt. % [9]. Studies of the electrical conductivity of nanomodified bitumen are entirely absent.

Therefore, in the current study, the most widespread, industrially produced and sensitive to electromagnetic radiation carbon nanostructures, such as multi-walled carbon nanotubes [11; 12] and graphene nanoplates [12–14] were selected as a filler for bitumen matrix.

The aim of the study is to develop the techniques of obtaining and studying the electrical characteristics of nanocomposites based on bitumen containing multi-walled carbon nanotubes (MWCNTs) and multilayer graphene nanoplates (MGs).

METHODS

Road bitumen of the BND 60/90 grade (OOO Ural Bitumen Plant, Yekaterinburg, Russia) was used as the base for the composites.

Bitumen was modified by “Taunite-M” MWCNT and “Taunite-GM” MG (OOO NanoTechCenter, Tambov, Russia). “Taunite-M” MWCNT are filamentary structures consisting of graphene layers with an internal channel. Their synthesis is carried out by chemical gas deposition. “Taunite-GM” MG is a two-dimensional graphene plates in the form of an aqueous paste. The dry residue content in the paste is 5–7 %. The parameters of “Taunite-M” MWCNT and “Taunite-GM” MG are given in Tables 1 and 2.

To eliminate aggregation and remove adsorbed water, MWCNTs were preliminarily dried in a vacuum furnace at 150 °C for 4 h. After drying, MWCNTs were mechanically activated in a WF-20B blade mill for 3 min at a rotation speed of a grinding body of 25000 rpm. This was done to reduce the size of agglomerates and improve the process of their dispersion in the polymer matrix, as was shown in [11].

MG in its original form was a water paste, which prevented its combination with bitumen. In this regard, MG was freeze-dried in a Scientz-10N dryer (Scientz, China) in two stages. At the first stage, the MG sample was frozen for 20 h to a temperature below −30 °C. Freezing was carried out until the temperature of the freezing chamber and the frozen sample equalized. At the second stage, the frozen sample was vacuum-treated for 20 h. After freeze-drying, MG was mechanically activated under the same conditions as MWCNTs.

To produce composite mixtures based on bitumen with MWCNTs (BCNT) and bitumen with MG (BMG), the following procedure was developed. Initially, the modifier was mixed with Nefras S2-80/120 gasoline (NK Rosneft, Russia) using a HT-120DX vertical rotary mixer (Daihan, Korea) and processed with I-10 ultrasound (Ultrasonic Technique – INLAB, Russia) within 30 min. Gasoline heated to 110 °C and lump bitumen were placed in a separate metal container. In such a way, bitumen co-melt and co-solution were obtained. The previously prepared dispersion of the modifier in gasoline was introduced into the resulting melt.

As part of the work, the authors designed a measuring cell to study the specific volume electrical resistivity of modified bitumen compositions (Fig. 1). Fig. 1 a shows the general view of the assembled measuring cell.

The cell (Fig. 1 b) consisted of measuring electrodes (1 and 2) made of foil fiberglass plastic, between which a fluoroplastic matrix (3) was installed. In the center of the matrix, there was a hole with a diameter of 6 mm.

The measurements were carried out as follows. At the first stage, the lower measuring electrode (2) was fastened to the matrix (3). The molten composite (4) was placed into the matrix hole, then, the upper measuring electrode (1) was installed on the assembly with the composite. The cell was tightened with screws and finger nuts, thereby forming a sample for measurement, which was a cylinder with a diameter of 6 mm and a height of 2 mm. The resistance of the samples was measured by connecting the upper and lower measuring electrodes to an E6-13A teraohmmeter (PunaneRet, Estonia) with an upper range limit of 10^{14} Ohm. The electrical conductivity was calculated according to the formula [15]:

$$\sigma = \frac{4h}{\pi d^2 R},$$

where h – studied sample height (cm);
d – studied sample diameter (cm);
R – electrical resistance (Ohm).

RESULTS

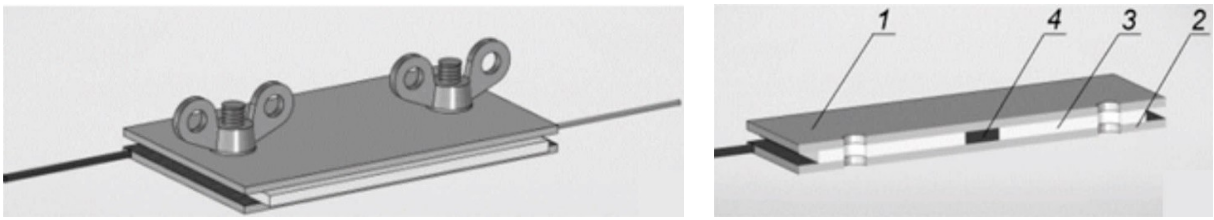
The electrical conductivity of the nanocomposites increased with increasing MWCNT mass content. The maximum electrical conductivity of 4.76×10^{-4} S/cm was achieved at 6 wt. % content of MWCNT in BCN, which is 3 orders of magnitude higher than the electrical conductivity of BMG nanocomposites containing 6 wt. % of MG (8.12×10^{-6} S/cm). In the case of using MG, the maximum electrical conductivity of 3.5×10^{-4} S/cm was observed in the BMG nanocomposite containing 11 wt. % (Fig. 2).

The results presented in Fig. 2 demonstrate that the dependence of the electrical conductivity of nanocomposites on the mass content has a percolation nature and is described by the expression [16]:

Table 1. *Characteristics of "Taunite-M" MWCNT and "Taunite-GM" MG [16]*

Characteristics	Taunite-M	Taunite-GM
Outer diameter, nm	10–30	–
Inner diameter, nm	5–15	–
Length, µm	≥2	–
Specific surface area, m^2/g	≥270	–
Pour density, g/cm^3	0.025–0.06	–
Number of graphene layers	–	15–25
Thickness of nanoplates, nm	–	6– 8
In-plane dimension of nanoplates, µm	–	2–10
Content of nanoplates, wt. %	–	4–7
Specific absorption rate, lm/(g·cm)	–	30–33

Note. Data of the company "NanoTechCenter" Ltd[1,2].



a ***b***

Fig. 1. *A cell for measuring specific volume resistivity:* ***a*** *– cell general view;* ***b*** *– cell in section.*
1, 2 – measuring electrodes; 3 – matrix; 4 – composite

[1] *CNT of "Taunite" series // NanoTechCenter. URL: http://www.nanotc.ru/producrions/87-cnm-taunit.*
[2] *Taunite GM" graphene // NanoTechCenter. URL: http://www.nanotc.ru/producrions/176-cnm-taunit-5.*

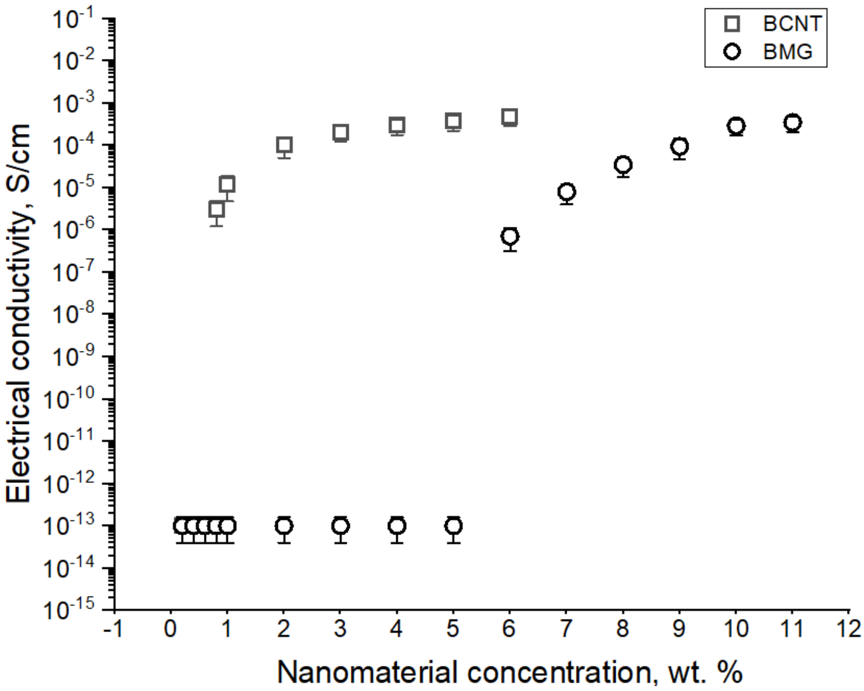


Fig. 2. *The dependences of specific volume electrical conductivity of bitumen-based nanocomposites on the carbon nanomaterial concentration*

$$\sigma = \sigma_f \left(\varphi - \varphi_c\right)^t , \quad (1)$$

where σ_f – MWCNT electrical conductivity;
φ_c – filler volume fraction corresponding to percolation threshold;
t – electrical conductivity critical value.

The obtained experimental electrical conductivity data are in good agreement with the theoretical values obtained according to formula (1) (Fig. 3). The correlation coefficients of the experimental and estimated curves for BCNT and BMG composites are equal to 0.99. The MWCNT volume fractions at the percolation threshold φ_c and electrical conductivity critical values t were determined using a linear regression of the *log*(σ) versus *log*(φ−φc) plot. For BCNT, φ_c and t were equal to 0.22 and 2.18, respectively (Fig. 3 a). For BMG, φ_c and t were equal to 0.63 and 3.20, respectively (Fig. 3 b). To form a percolation grid in a bitumen matrix, the MWCNT volume concentration of 2.8 times less than that of MG is required.

DISCUSSION

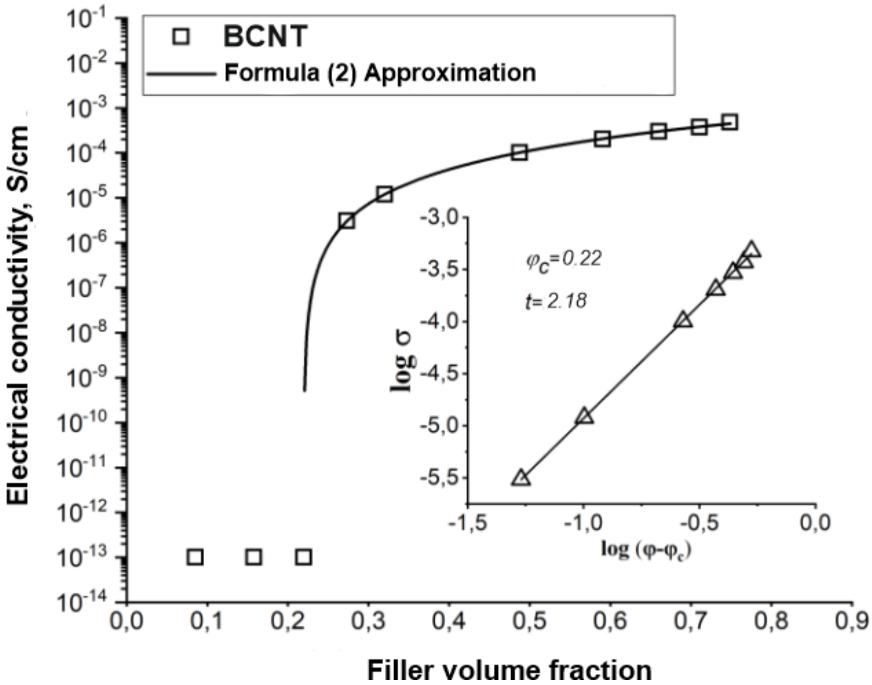
The values of the filler volume fraction at the percolation threshold, and the critical electrical conductivity values of the BCNT and BMG nanocomposites obtained, based on experimental data, create the prerequisites for the design and production of optimized bituminous compositions, with a given volume electrical conductivity, as well as those sensitive to microwave radiation.

Table 2 presents characteristics of fillers, variants of their distribution in the polymer matrix, and electrical conductivity parameters of nanocomposites obtained in this work and in other studies.

Composite materials modified with graphene nanoplatelets / epoxy resin and BMG with the same random filler distribution have higher values of the critical electrical conductivity (3.7 and 3.20, respectively) compared to MWCNT-based composites (Table 2). The filler volume fractions at the percolation threshold for the studied nanocomposites differ greatly from each other (3.2 and 0.63 vol. %, respectively). This is probably related to the fact that the graphene nanoplates used by the authors of [13] have a larger lateral size than the graphene from the present work. However, in the case of nanotubes, an opposite effect can be observed (Table 2). When using longer MWCNTs (10000–30000 μm), which were applied by the authors of [12] to create a polyethylene-based composition, the filler volume fraction at the percolation threshold is 4 times less than the value obtained in the study [15] for nanocomposites with short nanotubes (~2 μm). In all the cases considered, the formation of an infinite conducting cluster (percolation contour) in a polymer matrix requires a smaller amount of carbon nanotubes compared to graphene nanoplates, regardless of their structural characteristics and distribution pattern in the polymer matrix, as evidenced by the φ_c values (Table 2).

Thus, the electrical conductivity parameters (filler volume fraction at the percolation threshold, and the critical electrical conductivity value) are determined by the filler structural and morphological characteristics (filler particle size, filler particle type, etc.), as well as by the spatial distribution of particles in the polymer matrix.

The results of this study can become the basis for the birth of new ideas for the MWCNT and MG application as bitumen modifiers, focused on imparting electrically conductive properties to it. This, in turn, will contribute to expanding the range of its practical application as the main component for antistatic materials, conductive adhesive compositions, various repair and restoration compositions, road surfaces sensitive to microwave radiation. At the same



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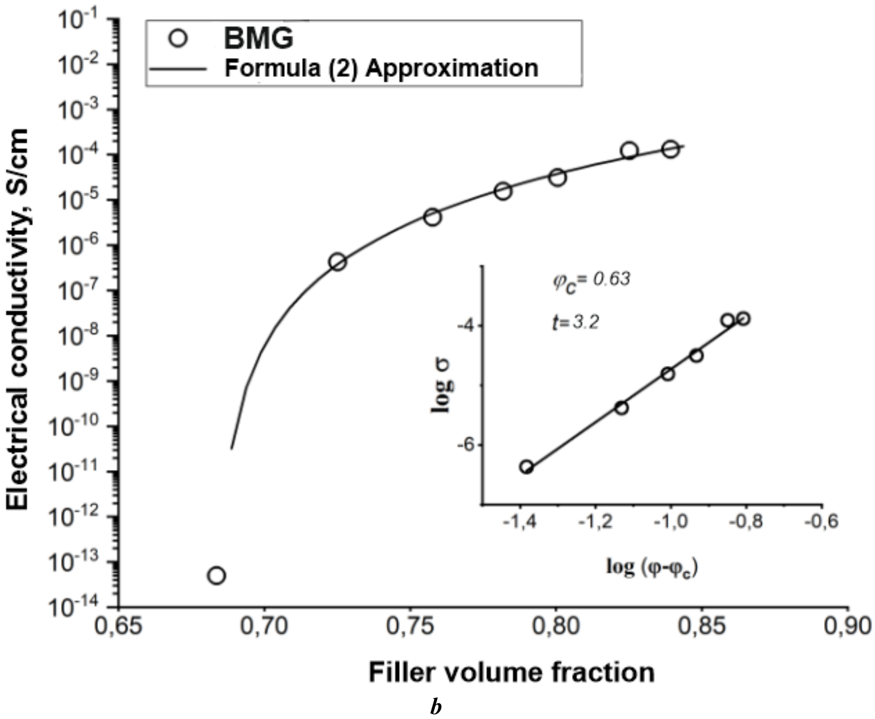

b

Fig. 3. *The dependence of specific volume electrical conductivity of nanocomposites on the filler concentration:*
***a** – BCNT; **b** – BMG.*
The inserts show the dependences of the electrical conductivity logarithm on the logarithm of the difference between the filler volume fraction and the filler volume fraction at the percolation threshold

Table 2. *Characteristics of fillers and polymeric nanocomposites on their base*

Filler type and its distribution pattern	Polymer matrix	Diameter, nm	Thickness, nm	Length, µm	φ_c, vol. %	*t*	Reference to work
Graphene nanoplates, over the boundaries of polymer particles	Polyethylene	200–30000	5–65	–	0.99	2.3	[12]
Carbon nanotubes, over the boundaries of polymer particles	Polyethylene	10–30	–	10000–30000	0.09	2.0	[12]
Graphene nanoplates, random distribution	Epoxy resin	200–30000	5–65	–	3.2	3.7	[13]
Carbon nanotubes, over the boundaries of polymer particles	Polymethyl-methacrylate	10–30	–	≥2	0.372	2.4	[15]
Carbon nanotubes, random distribution	Chloroprene rubber	10–30	–	≥2	0.232	2.16	[11]
Carbon nanotubes, random distribution	BND 60/90 grade bitumen	10–30	–	≥2	0.22	2.18	The results of this study
Graphene nanoplates, random distribution	BND 60/90 grade bitumen	2000–10000	6–8	–	0.63	3.20	The results of this study

time, the cumulative socio-economic effect of their use will exceed by orders the magnitude of a possible rise in the cost of these materials compared to conventional ones. For example, an increase in the inter-maintenance period of a road surface by 30 % gives a total effect that is 3 times higher than the entire cost of the materials used and the work. This occurs due to savings caused by reducing the work in complicated conditions, reducing the number of accidents, reducing the period of traffic restrictions and, as a result, leads to a decrease in the social tension level.

CONCLUSIONS

A technique for obtaining electrically conductive composites based on bitumen containing multi-walled carbon nanotubes, and multilayer graphene nanoplates was developed. Experimental conditions were created, and a technique was developed for measuring the specific volume resistivity of bitumen-based electrically conductive nanocomposites, containing multi-walled carbon nanotubes and multilayer graphene nanoplates. The information on the electrical characteristics of nanocomposites (specific electrical conductivity, volume fraction of the filler at the percolation threshold, electrical conductivity critical value) was obtained from the experimental dependences of the electrical conductivity of nanocomposites. The study established that the formation of a percolation grid in a bitumen matrix occurs at a lower volume content of MWCNTs compared to MG.

Thus, the application of electrically conductive BCNT and BMG nanocomposites with self-healing properties in special road surfaces, units, structures, and facilities will allow improving their reliability and inter-maintenance periods, which cannot be achieved by traditional methods without affecting all phase levels of the composite material.

REFERENCES

1. Zhu J., Birgisson B., Kringos N. Polymer modification of bitumen: Advances and challenges. *European Polymer Journal*, 2014, vol. 54, pp. 18–38. DOI: 10.1016/j.eurpolymj.2014.02.005.
2. Presti D.L. Recycled Tyre Rubber Modified Bitumens for road asphalt mixtures: A literature review. *Construction and Building Materials*, 2013, vol. 49, pp. 863–881. DOI: 10.1016/j.conbuildmat.2013.09.007.
3. Gulisano F., Gallego J. Microwave heating of asphalt paving materials: Principles, current status and next steps. *Construction and Building Materials*, 2021, vol. 278, article number 121993. DOI: 10.1016/j.conbuildmat.2020.121993.
4. Crucho J., Picado-Santos L., Neves J., Capitão S. A Review of Nanomaterials' Effecton Mechanical Performance and Aging of Asphalt Mixtures. *Applied Sciences*, 2019, vol. 9, no. 19, article number 3657. DOI: 10.3390/app9183657.
5. Wu Sh., Tahri O. State-of-art carbon and graphene family nanomaterials for asphalt modification. *Road Materials and Pavement Design*, 2019, vol. 22, no. 5, pp. 1–22. DOI: 10.1080/14680629.2019.1642946.
6. Latifi H., Hayati P. Evaluating the effects of the wet and simple processes for including carbon Nanotube modifier in hot mix asphalt. *Construction and Building Materials*, 2018, vol. 164, pp. 326–336. DOI: 10.1016/j.conbuildmat.2017.12.237.
7. Le J.L., Marasteanu M.O., Turos M. Mechanical and compaction properties of graphite nanoplatelet-modified asphalt binders and mixtures. *Road Materials and Pavement Design*, 2020, vol. 21, no. 5, pp. 1799–1814. DOI: 10.1080/14680629.2019.1567376.
8. Li C., Wu S., Chen Z., Tao G., Xiao Y. Improved microwave heating and healing properties of bitumen by using nanometer microwave-absorbers. *Construction*

and Building Materials, 2018, vol. 189, pp. 757–767. DOI: 10.1016/j.conbuildmat.2018.09.050.

9. Gulisano F., Crucho J., Gallego J., Picado-Santos L. Microwave healing performance of asphalt mixture containing electric arc furnace (EAF) slag and graphene nanoplatelets (GNPs). *Applied Sciences*, 2020, vol. 10, no. 4, article number 1428. DOI: 10.3390/app10041428.
10. Xu S., García A., Su J.-F., Liu Q., Tabaković A., Schlangen E. Self-Healing Asphalt Review: From Idea to Practice. *Advanced Materials Interfaces*, 2018, vol. 5, article number 1800536. DOI: 10.1002/admi.201800536.
11. Stolyarov R.A., Yagubov V.S., Memetova A.E., Memetov N.R., Tkachev A.G., Chapaksov N.A. Electrically conductive nanocomposites based on chloroprene rubber, containing multi-walled carbon nanotubes Taunit and Taunit-M. *Materialovedenie*, 2022, no. 5, pp. 41–48. EDN: DNHSIL.
12. Vovchenko L., Matzui L., Oliynyk V., Launets V., Mamunya Ye., Maruzhenko O. Nanocarbon/polyethylene composites with segregated conductive network for electromagnetic interference shielding. *Molecular Crystals and Liquid Crystals*, 2018, vol. 672, no. 1, pp. 186–198. DOI: 10.1080/15421406.2018.1555349.
13. Vovchenko L., Matzui L., Oliynyk V., Launetz V., Zagorodnii V., Lazarenko O. Chapter 2. Electrical and shielding properties of nanocarbon-epoxy composites. *Conductive Materials and Composites*. New York, Nova Science Publ., 2016, pp. 29–91.
14. Memetov N.R., Gerasimova A.V., Stolyarov R.A., Tkachev A.G., Melezhik A.V., Chapaksov N.A., Osipkov A.S., Mikhalev P.A., Provatorov A.S. Composite Materials Based on Foam Polyurethane and Graphene Nanoplates Effectively Screening Electromagnetic Radiation. *Advanced Materials and Technologies*, 2020, no. 17, pp. 68–73. DOI: 10.17277/amt.2020.01.pp.068-073.
15. Blokhin A., Stolyarov R., Burmistrov I. et al. Increasing electrical conductivity of PMMA-MWCNT composites by gas phase iodination. *Composites Science and Technology*, 2021, vol. 214, article number 108972. DOI: 10.1016/j.compscitech.2021.108972.
16. Mamunya E.P., Davidenko V.V., Lebedev E.V. Percolation conductivity of polymer composites filled with dispersed conductive filler. *Polymer composites*, 1995, vol. 16, no. 4, pp. 319–324. DOI: 10.1002/pc.750160409.