Theoretical and experimental researches of operating properties of bitumen reinforced with carbon nanotubes

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Abstract. The current level of economic development requires numerous road transport, which is constantly increasing, as a result, the roadbed is destroyed quite quickly. To maintain the durability of the road surface, various modifications are used to improve the physical properties. During the research, theoretical calculations and experimental confirmation of changes in the properties of bitumen when adding carbon nanotubes were carried out. Three concentrations of carbon nanotubes were tested: 0.1%, 0.01%, 0.001% in the bituminous mixture, as well as a reference sample without adding carbon nanotubes to compare changes in indicators. Based on the research carried out in the course of this work, it can be argued that the proposed method of strengthening the asphalt concrete coating by reinforcing the main component of the coating (bitumen) improves its physical and mechanical properties and, accordingly, increases the service life of the roadbed.

1. Introduction

To ensure the year-round movement of cars on the roadway, road clothing is arranged, which is a solid monolithic structure laid on the surface of the roadbed made of materials that resist the influence of climatic factors and the wheels of vehicles.

The current level of economic development requires numerous road transport, which is constantly increasing, as a result, the roadbed is destroyed quite quickly. To maintain the durability of the road surface, various modifications are used to improve the physical properties [1-3].

In most cases, asphalt concrete is chosen as a road surface because of its unique physical and mechanical properties, such as elasticity, resistance to long-term dynamic loads, wear resistance, and hydrophobicity. There are numerous mechanisms for improving the asphalt-concrete road surface [4, 5]. All these mechanisms are focused on changing the macrostructure of the roadbed, which requires a fairly large amount of new substances [6].

Nanotechnologies have been developing very rapidly over the past few years [7-10]. Nanotechnology-the science of manufacturing and properties of engineering elements at the atomic and molecular level-is currently one of the most interesting and attractive areas of science. Various structures and devices using nanotechnology are already included in our daily life [11-14]. The direction related to nanotubes and fullerenes, in particular, carbon nanotubes, is developing especially intensively. Carbon nanotubes are of particular interest because they can be used in electronics, composite materials, medicine, and even as storage for gases, metals, or liquids [1, 2, 7].
In this paper, we study the asphalt concrete coating, improved dispersion of carbon nanotubes in bitumen.

2. Experimental Researches
The bitumen was tested for three parameters:
1. Tensile test (at 25°C).
2. Viscosity test.
3. Softening temperature.

Three concentrations of carbon nanotubes were tested: 0.1%, 0.01%, 0.001% in a bitumen mixture, as well as a reference sample without adding carbon nanotubes to compare changes in indicators. Three measurements were made for each parameter and the standard deviation was determined.

Bitumen was heated on a sand bath, for more uniform heating. Bitumen, according to the study conditions, should not be heated above the critical temperature of 160 °C. The mixture was heated in the temperature range from 140 to 150 °C for at least an hour in order to get out of the solution all air bubbles that can distort the results of research.

Bitumen poured into molds cools in the air for half an hour for tensile and viscosity tests, and for an hour to determine the penetration index. In the future, the excess bitumen is removed from the top of the molds. Then the research blanks are placed in the environment that is specified in the standards for a specific research (Figures 1 - 3).

Figure 1. Determining the penetration index.  
Figure 2. Tensile testing of bitumen.  
Figure 3. The research of viscosity of bitumen.
3. Theoretical Researches

The density functional theory (DFT) method was chosen for theoretical calculations of the binding energy between the components of bitumen and carbon nanotubes. This method can be used in the Gaussian software package together with GaussView.

A naphthalene molecule (naphthalene) was selected from the bitumen components for calculations. Naphthalene is part of the paraffin-naphthene group of hydrocarbons, their content in bitumen can reach 60%. Naphthalene is also a structural unit of more complex bitumen molecules from the group of asphaltenes and resins that make up the main volume of hydrocarbons in the composition of bitumen.

The components of the calculation system were chosen: naphthene, without a single hydrogen atom; a hydrogen atom in the free state; a carbon nanotube of the "arm-chair" type (6,6). The assumption of a free hydrogen atom torn from the naphthene molecule can be made based on the assumption that bitumen is a viscous liquid in which such a phenomenon is likely.

Then theoretical calculations were made of a system consisting of: a carbon nanotube of the “arm-chair type” (6,6), a naphthene molecule (C_{10}H_8) without a single hydrogen atom and a hydrogen atom in a free state(Figures 4, 5).

The calculations were performed using the sequential approximation method. The method of sequential approximation consists in the fact that the nearest atoms of two or more components of the system are fixed at a given distance from each other and the total energy of the system is calculated for this position. For a full study of such calculations, there may be several dozen. In the future, after obtaining the dependence of the system energy on the distance between the components, normalization is performed. For normalization, the energy of individual components of the system is calculated and the sum of these energies is subtracted from the total energy value. As a result, the system interconnection energy is obtained, based on the values of which conclusions are made about the possibility or impossibility of the existence of a configuration of this system.

Figure 4. Model of interaction of a naphthene molecule, a hydrogen atom, and a carbon nanotube (6,6).
Calculations were performed in different geometric positions of the naphthene molecule relative to the carbon nanotube - with parallel and perpendicular orientation of the naphthene molecule.

4. Results and discussion
The results of experimental measurements are shown in Table 1, they show the dependence of the determined parameters (softening temperature, depth of penetration of the needle into the bituminous mixture and the length of stretching) on the percentage of carbon nanotubes in the mixture.

Table 1. Values of the studied parameters of the bitumen mixture depending on the content of carbon nanotubes, σ-standard deviation.

| Content of carbon nanotubes, % | Tensile test $\pm \sigma_{sm}$ | Viscosity test $\pm \sigma$ | Softening temperature $\pm \sigma^{0C}$ |
|-------------------------------|-------------------------------|--------------------------|--------------------------------------|
| 0.001%                        | 78±4                          | 51,25±1,299              | 46,25±0,2559                         |
| 0.01%                         | 133,5±7,5                     | 58±1,581                 | 45,75±0,2559                         |
| 0.1%                          | 148                           | 66,75±2,680              | 43,125±0,125                         |
| standard                      | 131,5±8,5                     | 68±1,224                 | 42,5±0,5                             |

As can be seen from Table 1, with the addition of carbon nanotubes to bitumen, its properties change. The softening temperature increases by 3.7 °C, which means that the bitumen becomes more fluid at a higher ambient temperature. This will allow the roadbed to resist the shear forces of car tires more strongly. The value of the penetration depth of the penetration needle decreases by 17 points. This means that the bitumen mixture becomes harder and stronger for external dynamic impact. Under vertical dynamic loads, the asphalt will be less deformed, and therefore less destroyed during operation. The only parameter that has undergone a negative change is the stretch. The stretching parameter reaches its best value at a concentration of 0.1% carbon nanotubes, and at 0.001% - the worst in this experiment. This parameter is important for coupling asphalt concrete mix components in
a heated state. At high temperatures, bitumen becomes very fluid and copes with its task regardless of the concentration of carbon nanotubes.

As a result of theoretical calculations, energy curves of the interaction of carbon nanotubes with a naphthene molecule were constructed.

Calculations have shown that the minimum binding energy, and, accordingly, the minimum potential energy of the system, is located at a distance of 1.9 Å from the surface of the nanotube with a perpendicular orientation of naphthene relative to the surface of the nanotube. This means that at this distance there is an adsorption interaction of the naphthene molecule with the surface of the carbon nanotube.

Thus, it can be argued that the mechanism of interaction between a carbon nanotube and a component of bitumen – naphthene – is the adsorption interaction of systems with a perpendicular orientation of naphthene relative to the surface of the nanotube. This system is energy-efficient, which will affect the quality of the new composition of bitumen with carbon nanotubes. This means that properties such as plasticity, wear resistance and adhesion will improve, which will lead to a longer service life of asphalt with the new bitumen composition.

5. Conclusion
It is established that the main mechanism for changing the properties of a mixture based on bitumen reinforced with a carbon nanomaterial is the adsorption interaction of the main components of bitumen (naphthene and anthracene) with the external surface of a carbon nanotube at a perpendicular location of the component molecule relative to the surface. Three main parameters of bitumen - penetration (needle penetration depth), extensibility and softening temperature - were tested for samples of a mixture with different content of carbon nanotubes: 0.1%, 0.01% and 0.001% by weight. It was found that two of the three key parameters improved, namely, the softening temperature increased, which will make the asphalt concrete more durable in hot climates, and the penetration decreased, which increases the wear resistance during operation. The amount of extensibility has decreased, which is quite logical, since when changing such characteristics as the softening temperature and penetration, the bitumen becomes harder and less viscous. Based on research, it can be argued that the proposed method of strengthening bitumen by reinforcing carbon nanotubes improves its physical and mechanical properties and, accordingly, increases its service life.

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