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Technology for improving modern polymer composite materials

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The purpose of the work was to determine the properties of the developed material (bitumen). In this study, the technological process was improved by modifying low-molecular weight butadiene and chloroprene rubbers structured with carbon nanotubes (CNTs) to obtain a material with the necessary set of desired properties. The article shows the possibility of modifying the bituminous binder of asphalt concrete with elastomeric rubbers structured with CNTs. The article also considers the use of promising polymer composite materials and the increase in their reliability and service life. Improvements in the properties of the composite and in the technology due to direct reinforcement with nanomaterials are described. The article defines the areas of application and recommended improvement of composite materials, as well as existing limitations.

Keywords: *polymer, composite materials, production technology, bitumen, nanomaterials*

1. Introduction

The factors that directly affect manufacture of polymer composite materials can be distinguished as follows:

- instability of the initially presented material characteristics;
- impact of different rates of the polymer formation on internal stresses in the product and directly their difference and unevenness;
- the occurrence of internal stresses under the influence of temperature, pressure, and other factors in the direct course of the manufacturing process;
- impact of a human factor on the desired physical, mechanical, and geometrical properties of the product, and errors in the formation of semi-finished composite materials;
- the use of product materials and shapes with initially different physical and mechanical characteristics.

An important feature in manufacture of polymer composite materials is the insufficient knowledge of the physicochemical properties of binders, prepregs, and polymer composite materials. The quality of the initial material has a significant impact on the resulting product [1]. Due to their adhesive properties, the surface quality and structure of fillers directly affect the mechanical characteristics of the developed materials. The architecture of fibrous materials, defects, their qualitative and quantitative composition also directly affect the properties of the applied carbon fillers [2]. An analysis of the features of physical and chemical formation processes shows that the polymer structure features determine the properties of polymer composite products. Internal stresses are manifested due to technological features and deformations caused by chemical reactions, as well as mechanical and physical processes and their direct interaction.

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Modern plasticizers represent specially synthesized surfactants based on polycarboxylate esters. In recent years, a new class of third-generation superplasticizers has been developed. It is based on hydrophilic copolymers of sulfates of (meth)acrylic acids and esters of (meth)acrylic acids, characterized by a lower dosage and higher reducing effect. They are also called polycarboxylate superplasticizers or hyperplasticizers, which were first found as a result of copolymerization of methacrylic acid with monomethacrylate of methoxy polyethylene glycol. It is possible to control polymer properties by increasing the length of the side chains and shortening the main chain. The study has shown that a polycarboxylate-based polymer plasticizer introduced into materials makes it possible to increase their strength and performance characteristics. However, polycarboxylate-based plasticizers do not always provide the required performance improvement. Therefore, researchers are currently working on the development of complex modifiers based on polycarboxylate esters.

The introduction of nanotechnological techniques is a progressive direction in the technology of building mixtures. These techniques imply the controlled material structure formation as a heterogeneous, multi-phase system of a complex hierarchy (from a nano- to a microstructural level) by modification of nano-sized particles in combination with high-performance polycarboxylate plasticizers. Carbon nanotubes (CNTs) are attracting increasing attention compared to other additive nanomodifiers that improve the properties of new materials. The introduction of multilayer CNTs into mixture compositions and bitumen can affect material properties if they have a diameter close to the thickness of the layers of nano-dispersed C-S-H phases. The study showed that multilayer nanotubes introduced into bitumen in small amounts increased the strength of the material, suggesting that CNTs have the potential to increase the strength of the material and represent centers more than reinforcement in the literal sense. These centers create conditions for newly formed crystalline structures, which grow, intertwine, partially merge, and design a spatial grid needed for binding the material. However, the ratio of CNTs to the volume of materials is sufficiently small (proportion of a percent), which causes some technological difficulties with their uniform distribution in the matrix.

The technical and technological quality of products made of polymer composite materials directly depend on the production technology, the optimal sequence of processes, and adherence to accuracy and regulations. It is necessary to initially model technological factors and consider the influence of temperature, the rate of heating and cooling, pressure, and holding time. Accordingly, theoretical aspects are needed, which show the dependence of these characteristics on technological factors and, due to this, generate control over the technical and accuracy characteristics of products [3]. Since the manufacturing process is very complex, strict control is necessary at each stage, in particular, for the parameters of temperature and humidity of the environment, raw materials, and materials used. A decrease in temperature by 1°C or an increase in humidity can lead to an increase in the polymerization time, which, in turn, can disrupt the entire technological chain of production [4]. In order to ensure the quality of products, it is necessary to monitor the kinetics of the processes that occur during the manufacture of a composite material, especially during the hardening of binders, depending on the technological modes, in particular the temperature and duration of exposure. For this, the characteristics should be first defined. Influence analysis of the following technological parameters of the manufacturing process of products from polymer composite is carried out materials:

1. Boundary limits are observed when the physical and chemical properties depend on the temperature at which molding takes place, and also when it depends on the time indicators of aging.
2. Factors affecting the curing time of the material during molding: (a) the chemical composition of the binder, (b) the catalyst used for chemical processes and the curing agent, (c) the thermophysical properties of the composite polymer, (d) the quality of the materials used, the size and shape of the

developed composite, the molding temperature, and (e) the effect of the curing time on the degree of binder hardening.

3. The type of filler and viscosity of the binder material directly affect the required pressure (its quantitative indicator). Compaction and additional penetration (impregnation) occur at the boundary values of the applied impact (pressure).
4. The heat capacity of the mold or material in contact, as well as the viscosity of binder materials, dictate the rate of heating of a given composite.
5. A high heating rate has a negative effect on the residual characteristics of the material. This often leads to uneven molding process, the formation of internal residual stresses, violation of the geometry, and volume of the material.

The stable and efficient functioning of the technological process directly depends on the successful process monitoring, which implements feedforward and feedback. The monitoring indicators help improve production technology by changing the parameters of the product molding stage [5]. In order to develop high-quality composites, the main direction of work should involve enhancing the shape accuracy of the reflective surface, increasing hardness, and reducing weight to improve the user properties of new-generation materials.

The purpose of the work is to determine the properties of the developed material (bitumen), in which the improvement of the technological process was carried out by modifying low-molecular weight butadiene and chloroprene rubbers structured with CNTs to obtain a material with the necessary set of desired properties. The following tasks were set to achieve the following purposes:

- to improve the properties of CNT-modified rubbers and their determination;
- to select the composition of the mixture using modified bitumen with rubbers structured by CNTs.

2. Materials and methods

The condition of the asphalt concrete pavement is continuously deteriorating on the entire pavement used due to the natural degradation (aging) of the roadway associated with an increase in traffic intensity due to an increase in the load from cars on the pavement itself, as well as the influence of classical weathering factors. Oil road bitumen is an essential component of asphalt concrete mixtures but is more susceptible to all types of deformations during processing. After the reconstruction of factories producing bitumen, it loses its unchanged properties, which leads to low-quality road bitumen; loss of crack resistance, elasticity, and adhesion; and premature deterioration of roads, bridges, and airfield asphalt concrete pavements [6].

The following two methods are used when obtaining bitumen from the quality aspect:

1. compounding method at the time of bitumen production;
2. modification of the properties of bituminous materials at the release stage.

These methods provide the necessary structural and mechanical properties at the stage of commercial product output. Since it is necessary to consider local technological aspects in addition to mixing by quality indicators, the use of combined mixing conditions is frequent. Compounding works by mixing multiple product streams into one. If there is no regulation or control during mixing, the values of oil quality indicators in the flow change over time and change in a particular range as a result of the reproduction of various pumping modes. In the case of controlled mixing, inherent flow instability is smoothed out by metered pumping of sour crude, which is prepared for blending, into the better quality oil stream in delivery directions where there is currently a margin of quality in accordance with the specific operational situation [7].

The authors considered the oil quality indicators used for bitumen production after various types of mixing and found that controlled mixing provided the reduced separation of sulfur and sulfur-containing substances in the stream. The homogeneity of characteristics increases with pre-

dictable and directly controlled mixing of oil. Simple uncontrolled mixing provides a non-uniform quality. Only controlled mixing of streams ensures consistent quality, guaranteeing optimal production of initial materials [8]. The methods that improve the quality and bitumen and its stability are as follows:

1. Physical methods that include mechanical and physical influence on the bitumen composition.
2. Chemical methods that imply changing the structure of bitumen by introducing various kinds of chemicals (additives).

The physical methods of modifying bitumen and ensuring its stable quality include the following: cavitation, ultrahigh-frequency (UHF) activation, ultrasonic treatment, and exposure to magnetic, acoustic, electromagnetic fields. The chemical method implies introducing additives during mixing. According to the literature, UHF units provide high efficiency when converting electromagnetic energy into thermal energy. It also ensures the ability to distribute energy evenly throughout the body of contact in the unit, its small size, the ability to vary in application and maintainability, and ease of maintenance [9].

The use of UHF units for modifying bitumen is a priority as it improves the physical, mechanical, and performance characteristics and durability of bitumen used in road and civil construction. The adhesive properties of bitumen increase because the connection with solid materials occurs through oxidation processes triggered by UHF waves. There is an increase in the strength of aromatic and heterocyclic structures, and the amount of aliphatic naphthenic and asphaltogenic acids increases [10]. The modified bitumen interacts differently with the solid parts of the developed material.

In the work by Lu and Isacsson [11], the use of microwave irradiation of bitumen significantly increases the structuring interaction with various fillers. At the same time, the internal ultimate stress increases, as shown by the instruments. This situation is primarily caused by internal rearrangements of bitumen molecules and their direct movement. Bitumen modified in this manner shows a progressive enhancement in performance due to changes in the physicotechnical and chemical properties of the components. This factor significantly affects the durability of the obtained materials.

In recent years, there has been increased interest in low-energy effects used to rebuild its structure without significant external energy consumption or the use of internal reserves of matter. Various types of electric, electromagnetic, magnetic, vibrational, or acoustic fields can be used as external influences, which affect the structure of substances, including oil-dispersed systems. At the same time, it is easy to achieve effects corresponding to an increase or, conversely, a decrease in order in the supramolecular structure of substances [12, 13].

Mineral additives are divided by constituent substances, chemical composition, and various activators. These minerals are as follows: asbestos, slag, cement, lime, limestone, phosphorus-containing, sulfur-containing, polyisobutylene, butadiene–styrene, and low-molecular weight organic amine, amide, amidoamine, imidazoline, and polymeric [14, 15].

According to Table 1 and literature data [16], adhesive additives are widely used. These additives directly improve the wetting of the surface of bitumen mineral materials, creating optimal conditions, forming an absorption layer that interacts between the constituent bitumen components. Such a factor reduces the temperature of the mixture and shortens the period for obtaining a homogeneous mixture, which, in turn, affects the intensity of bitumen aging and its destruction under the influence of natural factors [14]. Separately, it is worth considering polymer additives. To obtain polymer bituminous binders, various devices are used, such as paddle mixers, colloid mills, and hydrodynamic mixers. Polymer-bituminous binders (PBBs) are in high demand, and choosing the right PBBs allows using a coating based on it for up to 20 years. Modification of bitumen also depends on the composition of the polymer used; in practical use, the availability and low cost of the polymer also play a role.

Modification of bitumen with elastomeric materials like rubbers also plays a decisive role. The

Table 1. Classification of modifying additives for bitumen

Modifying additive	Plasticizing		Structuring	Adhesive	Temperature improvers
Polyimproved compounds	LM	+			
	PV		+		+
	LMWP	+			+
	BSC		+		+
	DST	+		+	
	PVB		+		+
	PPR	+			
	R + HPT	+		+	+
	LMWAA-A		+	+	+
	LMWAA-B		+	+	+
Surfactants	DEG	+		+	+
	TEG	+		+	+
	MEA	+		+	
	DEA	+		+	+
	BSU	+		+	
	Additive adhesive BP-3M	+		+	
	ORSK-superplasticizer		+		

BSC, butadiene–styrene caoutchouc; BSU, butadiene–styrene; DEA, diethanolamine; DEG, diethylene glycol; DST, divinyl styrene; LM, low molecular; LMWAA-A, low-molecular weight antifreeze additive A; LMWAA-B, low-molecular weight antifreeze additive B; LMWP, low-molecular weight polyethylene; MEA, monoethylamine; PPR, petroleum–polymer resin; PV, polyvinyl; PVB, polyvinyl butyral; R + HPT, waste rubber and heavy pyrolysis tar

Table 2. Properties of CNT made of fly ash

Indicator	Physical and mechanical properties of fiber of fly ash
Average fiber diameter, μm	1–15.0
Non-fibrous additives, %	2–3
Density, g/cm^3	2.65
Temperature, °C	−269 to +700
Water resistance, %	99.6
Chemical resistance, %	93.4 77.3 98.5
0.5H NaOH	
2H NaOH	
2H H_2SO_4	
Hygroscopicity, %	$\leq$ 1.0
Mechanical strength, MPa	4,100
Modulus of elasticity, MPa	120
Elongation at break, %	3.1

CNT, carbon nanotube

use of nanomodified materials is promising too. Nanomodifiers play the role of adsorbents, catalysts, and chemical reaction modifiers, technologically and constructively improving the properties of manufactured materials [17]. The use of such modifiers is a solution to the main problem in the production of building materials—energy-saving and reduction of the technogenic impact of the building materials industry on the environment.

Sun and Sheng [18], Xu et al. [19], Pan et al. [20], and Golestani et al. [21] considered the questions related to the assessment and selection of modifiers and their applications in road construction. The use of CNTs in the production of liq-

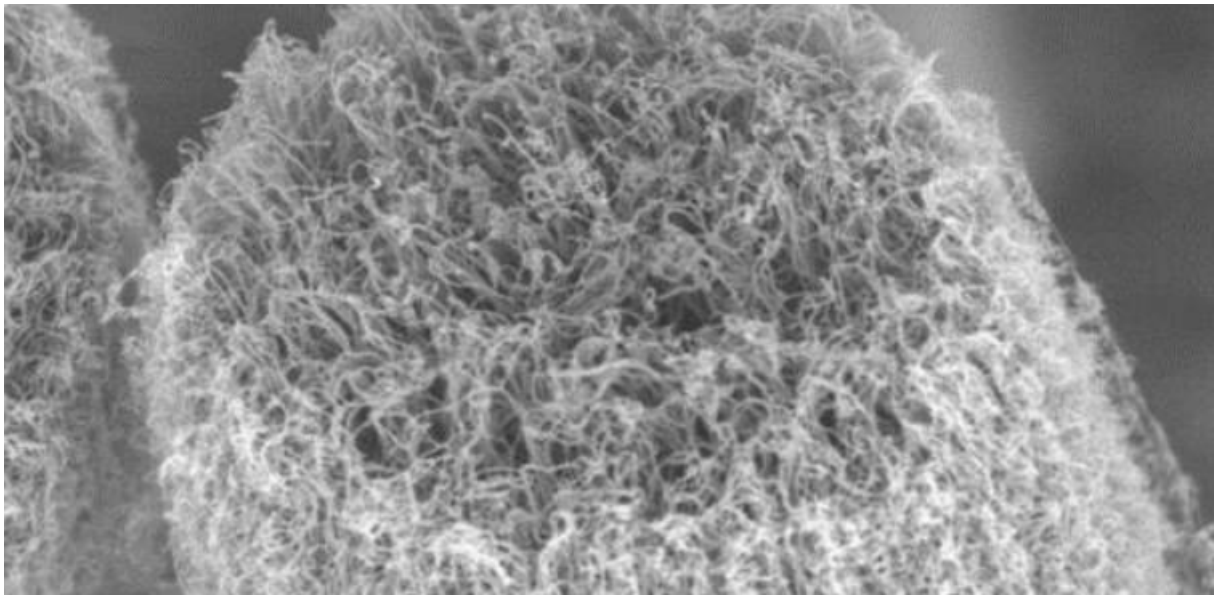


Fig. 1. Standard CNTs. CNTs, carbon nanotubes

uid bitumen increases the strength and deformative properties of the resulting final product. It has been empirically proven that the addition of CNT additives of 0.005 wt.% increases the compressive strength of bitumen [22].

It is known that CNT is a highly efficient filler; hence, a continuous CNT network is formed in the polymer matrix at a concentration of 0.1 wt.% with a homogeneous distribution [23]. In this case, the properties change significantly: the composite acquires high electrical and thermal conductivity, and the elastic modulus, conditional yield strength, wear resistance, etc. increase. Therefore, it is necessary to study the characteristics of CNT agglomerates and search for an effective method for their dispersion and separation.

Thus, achieving a uniform distribution in the matrix is a precondition for the effective operation of CNTs because the tendency of nanotubes to aggregate prevents high degrees of dispersion. To improve the properties of organic binders such as petroleum road bitumen, various modifiers are used: polymers including plastics and rubbers, surface active substances (SAS), antioxidants, anti-advisers, biocides, and fungicides. As a rule, they all have a positive effect on certain properties. But at the same time, they also have a negative impact, if not directly on the properties of the binder, then indirectly on the properties of asphalt concrete or on the technological process of preparing and laying asphalt. Therefore, modifiers should not be considered as a super means for improving the whole complex of bitumen properties. It is necessary to investigate the effect of modifiers different in chemical composition and nature and use the obtained data in cases of improving certain properties of the binder.

3. Results and discussion

Modification of butadiene caoutchouc and their study

We chose NBR-18 (natural rubber NBR polyamide) as a basis and varied the amount of multilayer carbon nanotubes (ML CNTs) introduced. The mixing of caoutchouc with components of rubber compounds that have a different shape, size, state of aggregation, different solubility, and speed of distribution not only in caoutchouc but also in the material being modified is a complex technical problem that must be solved primarily theoretically, predicting and controlling the process of manufacturing.

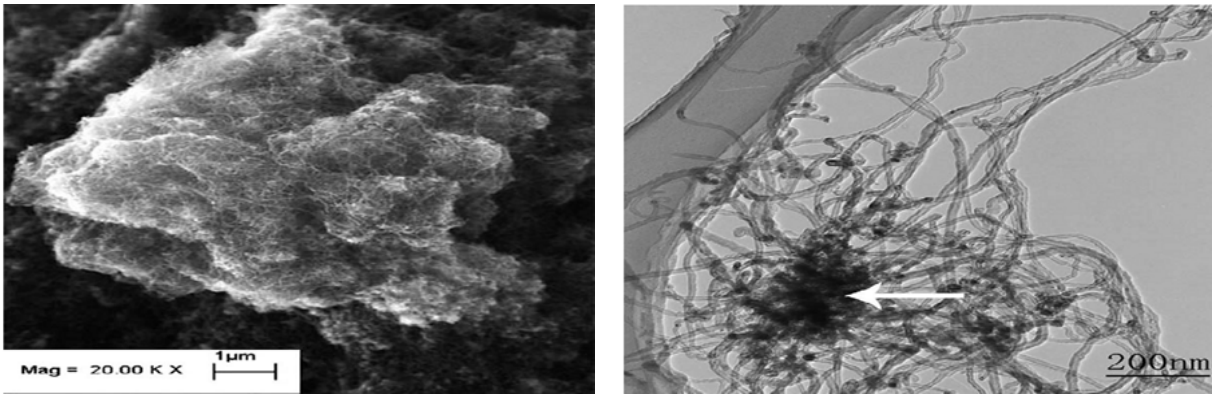


Fig. 2. Agglomerates of ML CNTs obtained by the CCVD method. ML CNTs, multilayer carbon nanotubes

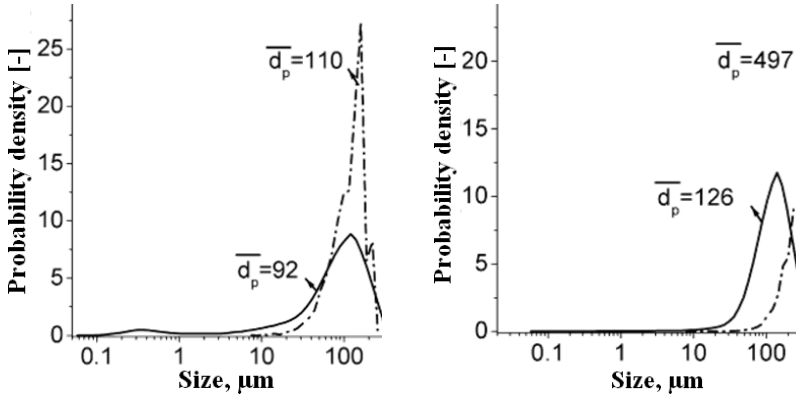


Fig. 3. Comparison of particle sizes determined by laser scanning and the method of statistical processing of microphotographs (— laser scanning, -•-•- microphotographs statistics): **(A)** starting catalyst particles and **(B)** ML CNT agglomerates. ML CNT, multilayer carbon nanotube

The introduction of high-dispersed carbon nanomaterials is difficult in terms of uniform placement of additives (its quantitative ratio to total volume is usually small) in the elastomeric composition. The correct distribution of the physicochemical characteristics of the mixture is achieved only with a uniform distribution of the designed (modified) material components. The obtained multilayer propylene CNTs corresponded to TU U 24.1-03291669-009:2008 and had the following parameters (they were obtained by the catalytic decomposition method):

- average diameter – 10–20 nm;
- specific surface – 200–500 m^2/h;
- bulk density – 15–40 g/dm^3;
- content of mineral residue: crude – 6%–20%,
- purified – <1%;
- temperature of the 5% mass loss after purification of mineral impurities – 520–620°C;
- the specific electrical resistance of the compressed powder of nanotubes purified from mineral impurities – 0.05–0.15 Ωcm.

Characteristics of CNTs were determined by using the following methods: transmission microscopy (JEM-100CXII), X-ray diffraction (DRON-3M, λCo = 0.179 nm), combinatorial scattering (Brucker RFS 100/s spectrometer), and radiation source–4.5 differential thermal and gravimetric analysis (derivatograph Q 1500, heating rate

Table 3. Composition of rubber and CNT

Sample	NR, g	BR9000, g	CNT, % (by weight of rubber)	CNT, g	N220, g
S-0	1,330	224	0	0	666.4
S-1*	1,330	224	0.65	9.7	656.7
S-2**	1,330	224	0.65	9.7	656.7
S-3	1,330	224	2.5	38.8	627.6
S-4	1,330	224	1.25	19.4	647
S-5	1,330	224	0.65	9.7	656.7
S-6	1,330	224	0.325	4.8	661.6
S-8	1,330	224	0.16	2.4	664
S-9***	1,330	224	0.65	9.7	656.7
S-7	1,330	224	20	310.8	0

CNT, carbon nanotube.
*–soot and CNT dispersions were prepared separately (for each 10 min of ultrasonic dispersion) and then mixed.
**–soot was simply mixed with CNTs in a dry form (without dispersion).
***–spraying according to the standard scheme, but with the addition of rosin to alcohol (0.5 mass parts = 7 g)

10 K/min). The CNT surface was characterized by X-ray photoelectron spectroscopy (XPS) (spectrometer "SERIES 800 XPS" Kratos Analytical, X-ray source MgK – 1,253.6 eV). The line profile analysis of the XPS spectrum was carried out using the XPSPEAK 95 program, version 2, using a mixed Gaussian–Lorentzian distribution function. Large-scale production of CNTs, usually within the CCVD method, produces VNTs in the form of derivative tubes that are intertwined with each other with dimensions of 20–500° μm (Figure 2).

As can be seen from Figure 3, the size distribution of ML CNT agglomerates, to some extent, repeats, respectively, the distribution of catalyst particles.

The caoutchouc mixture is produced on cold rollers for 20 min at temperatures <60°C. To assess the strength of the properties on the basis of the obtained compositions, rubbers were made in a vulcanization press at 153°C for 30 min. The scheme for obtaining composite polymers filled with CNTs is shown in Figure 4.

Method and scheme for the rubber mixture preparation:

1. Warming up the mixer to 60°C.
2. Loading rubbers.
3. Plastification and mixing of rubbers – 10 min.

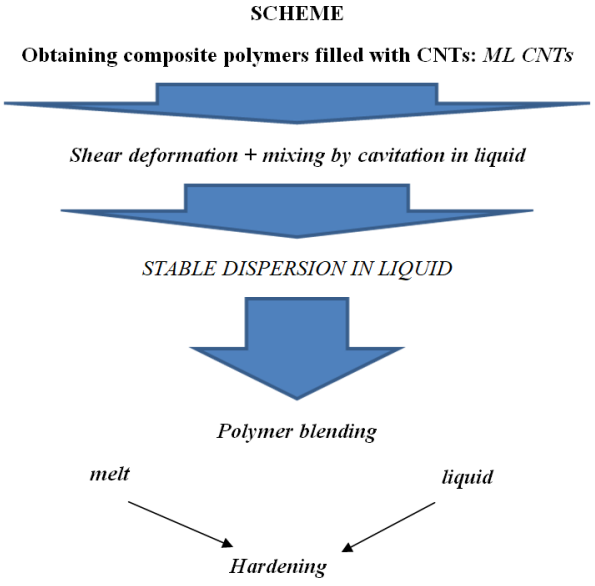


Fig. 4. Scheme for obtaining composite polymers filled with CNTs. CNTs, carbon nanotubes; ML CNTs, multilayer carbon nanotubes

4. Addition of CNTs.
5. Mixing and dispersion – 20 min.
6. Unloading the mixture.

3.1. Dispersion preparation

In a glass 15–20 min dispersion of CNTs with an ultrasonic disperser in a solution of isopropyl alcohol (until the alcohol boils), then the addition

Table 4. Measured data of the experimental results

Sample	**Hardness, A, relative units**	**Boundary tensile strength, MPa**		**Relative elongation at break, %**		**Break, %**	
		21.8		539		12.863	
		18.3		479		10.534	
S_0	61	19.7	19.7	483	486	12.043	12.043
		20.2		504		13.337	
		19.3		486		10.416	
		24.6		470		6.983	
		23.4		490		8.384	
S_1	63	23.6	23.4	483	483	11.762	8.384
		22.9		494		9.653	
		22.7		448		6.867	
		22.3		449		7.286	
		22.4		487		10.289	
S_2	65	23.1	22.3	492	478	10.079	9.53
		22.4		478		8.686	
		22.3		429		9.53	
		22		485		9.089	
		21.1		478		6.74	
S_3	62	20.5	20.5	486	486	9.576	9.089
		19.9		499		11.099	
		19.7		494		8.991	
		23.4		471		9.399	
		24.5		502		6.896	
S_4	63	24.6	24.2	519	501	7.52	7.52
		22.8		465		7.832	
		24.2		501		6.283	
		24.5		503		\	
		22.7		470		8.693	
S_5	62	24	23.6	511	491	8.259	8.1
		23.1		480		7.541	
		23.6		491		7.899	
		24.9		514		7.426	
		24.4		520		8.298	
S_6	65	23.6	23.6	476	514	7.612	7.426
		23.7		538		6.513	
		23.7		507		7.393	
		24.5		487		9.484	
		24.8		493		6.696	
S_8	65	24.4	24.4	446	476	8.997	8.997
		24.2		476		6.521	
		23.8		452		10.213	
		24.1		556		8.615	
		22.6		489		13.937	
S_9	66	21.9	22.6	462	505	11.319	11.319
		22.4		519		11.497	
		22.8		505		11.274	

Table 5. Results of the study on aging and wear resistance

Samples	S0	S1	S2	S3	S4	S5	S6	S8	S9
	Vulcanization 150°C×30′								
Hardness A, rel.un.	61	63	65	62	63	62	65	65	61
Boundary tensile strength, MPa	19.7	23.4	22.4	20.5	24.2	23.6	23.6	24.4	22.6
Relative elongation at break, %	486	483	478	486	501	491	514	476	505
	100°C*168 h Aging								
Hardness A, rel.un.	62	65	68	64	67	62	67	64	65
Boundary tensile strength, MPa	12.4	14.2	14.2	12.3	15.9	14.6	16.7	16.4	13.7
Relative elongation at break, %	349	314	295	326	332	338	357	326	339
Wear resistance, J/mm^3	98	102	100	94	92	103	100	93	105

Test results correspond to GOST 27674-88

Table 6. Sample test results

MWCNT, wt.%	**Breaking strength, MPa**	**Elongation at break, %**	**Compressive strength, MPa**	**Shore hardness, c.od.**
0	19.7	486	12	61
0.16	24.4	476	9	65
0.325	23.6	514	7.4	65
0.65	23.6	491	8.1	62
1.25	24.2	501	7.5	63
2.5	20.5	486	9.1	62

of soot in small portions with constant stirring, and another 10 min of joint dispersion with ultrasound. After that, the alcohol bulk was distilled in a rotary vacuum evaporator at 80°C and subsequently dried in a vacuum oven at 125°C.

The measurements of the obtained samples are presented in Table 4.

The results showed that the introduction of 0.16–0.65°wt.% MWCNTs (multiwalled carbon nanotubes) into the composition leads to an increase in the physicomechanical parameters (samples S5–S8). The maximum conditional strength and maximum relative elongation result in a composite with a content of 0.325°wt.h MWCNT. A composite of this composition has the highest bond energy in the polymer matrix. With a further increase in the content of MWCNTs up to 5°wt.h., physical and mechanical parameters decrease, that is, the bond energy in the polymer matrix is gradually destroyed. Dependences of conditional strength and relative elongation at break on masses of the introduced MWCNT are shown in Tables 4–6.

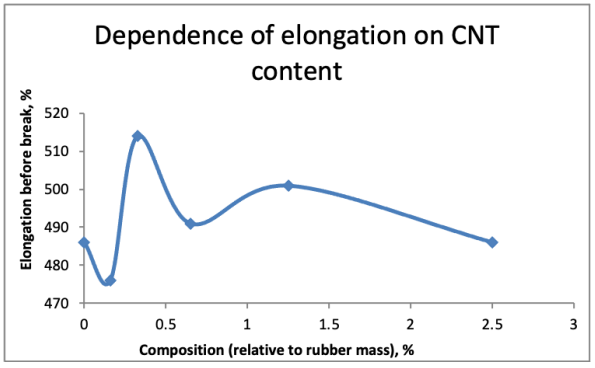


Fig. 5. Dependence of the elongation at break of the butadiene–nitrile composite on the MWCNT content

Thus, according to the obtained experimental dependences, 0.365 wt.% MWCNTs introduced give maximum values of the physical and mechanical properties of the rubber mixture. With further introduction of MWCNTs, a decrease in the relative strength and relative elongation at break was observed. This is due to the destruction of bonds in the elastomeric composition.

Table 7. Physical and mechanical characteristics of bitumen (original and modified)

Bitumen 90/130 with additive, wt.%	Temperature, °C		Plasticity interval, Pa	Needle penetration depth at 25°C/0°C, 0.1 mm	Stretch at 25°C/0°C, cm	Elasticity at 25°C, %	Surface grip
	Fragility to Fraasu	Softening according to KiSh					
0	−21	44	65	124/29	57/5.6	5	Fair
2	−25	47	72	126/32	78/18	27	Good
3	−31	48	79	128/35	86/28	46	Excellent
4	−37	52	89	130/42	?100/34	57	Excellent
8	−24	54	78	162/83	77/33	28	Fair

The impact of rubber modifiers on the performance properties of binder asphalt concrete. Table 7 shows the experimental results of modifying the bituminous binder with rubbers structured with CNTs.

As can be seen from the data in Table 6, a quantitative composition of 4% by mass is the optimum composition of rubbers structured by CNTs in bitumen. This amount of additive resulted in a decrease in the brittleness temperature, which made it possible to achieve large negative values and, as a result, increase the frost resistance of the binder and materials made from it. The softening temperatures of 52°C and 64°C obtained experimentally are much higher than the declared characteristics of existing additives. This fact shows an increase in the heat resistance of products made from the modified binder. When using 4% content of SKN-30 KTRA in the experiments, the penetration P25 at 25°C (depth of the needle penetration into bitumen at 25°C) complies with the P25 standards for concrete grade BND 90/130. Accordingly, the process of obtaining asphalt concrete mixtures and other bitumen-based materials will take place in a regulated manner [24].

According to this finding, the considered elastomeric rubbers structured with CNTs with the composition of 4% by mass show a significant increase in all physical, mechanical, and performance properties of the binder [25]. The use of nanomaterials is the area in which improvement is recommended due to the existing limitations. It is possible to directly consider the scope of nanomaterials based on the analysis of relatively recent literature. Apart from that, consideration of prior literature can provide some solutions and ideas that were seen as irrelevant for some period of time due to various factors [26]. It is reasonable to assume that the usual literature review of the nanomaterial application fields may not completely show the picture. However, although being of a theoretical nature, such studies can give the necessary idea of the prospects for the use of nanomaterials and demonstrate the trends in the rational use of composite nanomodified materials.

The use of carbon nanomodifiers in structural materials gives bulk materials and structures greater strength under static loads. In contrast to metals, such materials have less signs of fatigue and aging, while the weathering processes are minimized [27]. Moreover, they demonstrate greater hardness than materials with conventional deformation properties. Therefore, currently, high-strength and wear-resistant structural materials are the most promising and expedient nanomodified polymer composite materials. In the materials under consideration (polymer composites), the yield strength increases by 2.5–3 times compared with conventional unmodified materials, while the elasticity in some cases remains unchanged. However, it increases by more than four times for Ni_3Al [28]. Composite nanomaterials reinforced with carbon nanofibers and fullerenes can be used for the military field and in the manufacture of light aircraft parts. They can also be promising materials for working under conditions of striking dynamic actions, including armors, body armor vests, and load-bearing structures of transport units.

Such composite nanomaterials can be also applied as tool materials. Tool alloys with polymer

composites or with carbon nanomaterials are used in the manufacture of many tools. Moreover, metal nanopowders with inclusions of carbides, compressed carbons, and other abrasive components are used as a grinding and polishing material for the processing of semiconductors and dielectrics and high-precision polishing of metals that require stripping elements [29].

Furthermore, they are used in manufacturing technologies. The use of nanomodified polymeric materials in production is resourceful. The components of the composites themselves in most cases consist of nanomaterials (carbon nanomodifiers, fiber derivatives, and nanotubes have many advantages). The range of their application is very wide, while their purpose is versatile. In the production of steel and its alloys, the introduction of nanopowders (charging) to conventional powders makes it possible to reduce the porosity of products and improve the complex of mechanical properties [30]. In powder metallurgy, the addition of polymers increases the efficiency of the resulting composites compared to the standard materials, and the composites are not only similar to metals obtained by classical methods but also significantly exceed them in many cases in terms of the characteristics such as hardness and strength.

The addition of polymers and carbon nanomaterials to aluminum and titanium nanostructured alloys results in superplasticity in the resulting composites, which can be used for the manufacture of parts and complex shape products. They can also be used as bonding layers for welding various materials in the solid state. The presence of a large specific surface area of the applied polymeric and nanomaterials (about $5 \times 107\ m^{-1}$) makes it possible to regard their use as catalysts in chemical production and the agricultural sector [31].

The use of nanomodified composite materials in the nuclear power industry is also significant. In the United States and some European countries, nanomodified composite materials are used in the absorption of high-frequency and X-ray radiation. Besides, vermiculite and vermiculite-containing micas are directly used in modified materials to absorb radiation (alpha and beta particles) and as a powerful heat-insulating material. Fuel pellets are made from ultrafine UO_2 powders. In thermonuclear technology, composite materials are used as a target for laser thermonuclear fusion from ultrafine beryllium [32]. Gloves, aprons, and other protective clothing made of rubberized polymeric artificial materials with the addition of ultrafine lead fillers with the same protective measures is four times lighter than ordinary protective clothing. Accordingly, the use of protective gloves, aprons, and overalls with ultrafine lead and vermiculite filler not only increases labor productivity and reduces fatigue but also increases radiation and thermal protection.

Nanomodified composite materials are also applied in electronic engineering and electromagnetic installations. The extended machine performance composition of some nanomaterials (iron in combination with chalcogenide layers) is used in the recovery industry [33]. Film nanomaterials with a flat surface and a complex surface shape significantly outperform traditional materials. Thus, CNTs, filled with carbides of refractory metals (TAC, NBC, and MOC) can be used as superconductors by the deposition of lithium on a porous substrate of aluminum oxide nanowires of Fe 0.3 Co 0.7 alloy with a diameter of 50 nm [34]. Moreover, fullerenes and fullerene-based composite nanomaterials are promising materials for manufacture of various kinds of optical and photoelectric materials [35–44].

4. Conclusion

The factors influencing the quality of manufacturing products from polymer composite materials are discussed in this article. The indicators characterizing the kinetics of a composite material process are considered. The technological parameters of the manufacturing process from polymer composite materials are analyzed. The possibility of modifying bituminous binder asphalt concrete with elastomeric rubbers structured with CNTs is considered in the article. The use of modifiers based on rubbers structured with CNTs containing 4% by mass increases the physical and mechanical properties of the modified nanomaterial (in the case of a binder) to a large extent. The main areas of

nanomaterial application and possible limitations are considered.

The use of promising polymer composite materials and the increase in their reliability and service life are substantiated. Improvements in the properties of the composite and improvement of technology due to direct reinforcement with nanomaterials are shown. The areas of application and recommended improvement of composite materials, and the existing limitations are considered as well.

The authors of this article examined the areas of application and recommended improvement of composite materials. The study also considered the existing limitations of modification of low-molecular weight butadiene and chloroprene rubbers structured with CNTs. As a result, the material with the enhanced complex of desired properties was developed. The properties of rubbers modified with CNTs were enhanced, and the optimum compositions were developed based on rubber-modified bitumen structured with CNTs.

An analysis of the application areas showed that improvement is necessary in almost all areas affecting both heavy and light industries, including structural production, tool production, heavy industry, metallurgy, nuclear power, electronics, electromagnetic industry, and military industry.

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