

Features of interaction of carbon primary nanoscale materials with hydrocarbon plasticizers for quality management of polymer modified binders

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Abstract. In present time building materials science is increasingly considering the basic properties of substances, the parameters of phenomena and processes involved in the formation of materials on a nanoscale scale. Carbon nanomaterials due to their structural and energy characteristics, unique mechanical, thermal and optical properties are of increased interest not only as an object of scientific research. But also as an object of technology that provides control of the structure formation of the composite and giving it a level of quality. Phenomena and processes related to the behavior of multilayer carbon nanotubes in hydrocarbon media are considered. Based on the Traxler coefficient a forecast of the type of plasticizer with maximum compatibility with carbon multilayer tubes was carried out. The relationship between the molecular weight of hydrocarbon plasticizers and the concentration of carbon primary nanomaterials in the studied systems on the dispersing ability and stabilizing effect of the medium has been established. The features of the interaction of carbon nanotubes with hydrocarbon plasticizers and their effect on the properties of polymer modified binders were shown.

1 Introduction

The obvious reasons for premature wear of road surfaces under the influence of increased traffic intensity and increased axial loads of motor transport are the poor quality of the components used, imperfection of methods for designing asphalt concrete and road compositions, insufficient quality of asphalt concrete coating manufacturing technology. The introduction of carbon nanomaterials as modifiers with the use of various plasticizers is a promising direction in materials science to increase the durability of asphalt concrete.

Carbon nanomaterials, due to their unusual structure and unique mechanical, thermal and optical properties, are of increased interest in areas of various scientific levels. Numerous studies of their production methods have led to the creation of various types of carbon nanomaterials, which differ in their properties and structure, among them the most

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relevant are multi-walled carbon nanotubes, which is also evidenced by their production on an industrial scale. In [1-3] it was found that multi-walled carbon nanotubes have good self-lubricating characteristics. And high mechanical characteristics, thermal stability and resistance to oxidation allow increasing the further preservation of their properties during friction. The authors of [4, 5] have studied some properties of CNTs and proved that they can withstand thousands of cycles of "stretching – compression" without accumulation of fatigue and rupture. Researchers [6-10] studied structures similar to graphenes and obtained images using a transmission electron microscope, where curved "sheets" were present, separated from the destroyed multilayer "bulbs" of fullerenes. According to other researchers [11-14], the concentration of fullerenes in natural solid bitumen is 0.2-0.3 ppm, the remaining fullerenes are practically absent. Thus, in the field of "oil and gas nanotechnology", of particular interest is the ability of primary nanostructures to form various molecular aggregates (nanocolloids) in a variety of organic solvents, including natural oils and bitumen. The paper [15] presents a nanostructuring modifier for asphalt concrete containing several types of nanostructures, such as nanotubes, carbon black and organocline. the addition of the proposed modifier in the amount of 0.1% of the total mass of asphalt concrete allows to increase the strength of asphalt concrete under compression by 50%, and frost resistance by 20%. However, the effectiveness of the introduction of nanoparticles significantly depends not only on their type, dosage, but also on the technological parameters of modification. In a number of works by scientists from China [16-19], a positive effect of modifying asphalt concrete mixtures with a complex modifier based on SBS and nanoparticles is noted. It is noted in [20, 21] that high efficiency without significant economic costs in the production of asphalt concrete can be achieved through the integrated use of polymers of various groups and secondary raw materials (substandard mineral materials, industrial waste). It is noted that the positive effects are significantly enhanced when using nanometer-sized components. However, the authors do not offer solutions to the problem of their dispersion in volume. Ssh Ping Wu, Liu Gong, Jin Gang Bang [22, 23] investigated the effect of nanocline on the properties of polymer modified bitumen (PMB). Morphological studies have shown that dispersed polymer particles existed in a continuous phase of bitumen and the addition of nanocline did not change the size of polymer particles. The use of complex polymer additives and nanoparticles proceeds with the formation of a special polymer structure at the nano- and micro-levels under the influence of nanomodifying microparticles. In the works of Luz, S Quintero, Luis E Sanabria [24], the possibility of using substandard TU as a modifying additive to road bitumen, a structure-forming additive to oil tar and liquid residual bitumen, as well as a filler for organomineral compositions was analyzed. Due to the large specific surface area, developed porous structure and high adsorption capacity, carbon nanomaterials are widely used in gas purification, therefore they are widely studied for gas systems and there are practically no works studying the features of interaction with liquids. Thus, in [25, 26], the processes of acetone adsorption on the surface of carbon metal-containing nanostructures were investigated. As a result of the work carried out, it was found that in the case of adsorption of polyatomic molecules such as acetone, the final result of the process will depend not only on temperature, pressure, surface shape, but also on the spatial orientation of the adsorbate molecule relative to the surface of the adsorbent, as well as the surface tension of the liquid containing acetone in ketone and phenolic forms and products of its interaction with a sample. Thus, the authors themselves conclude that the established results on the adsorption of liquid acetone cannot provide information about the absolute values of the sorption capacity of the samples. The authors [27-30] performed quantum chemical studies of the adsorption processes of heavy alcohol molecules (normal and isomeric propanol) on the outer surface of single-layer carbon nanotubes. The possibility of physical adsorption is proved. Experimental studies of their sorption activity in relation to organic

compounds have been carried out. The positive effect of CNT on the purification process of individual products of the distillery industry has been proven. Thus, summarizing the international research experience [1-30], it can be concluded that, despite certain difficulties in designing and obtaining new nanomodified materials for road construction with a complex of unique properties, this area of building materials science is promising, but little studied and little developed. Knowledge of the patterns of surface phenomena in dispersed systems of various types, methods of obtaining, stabilizing and destroying these systems, as well as their physico-chemical properties is necessary for effective control of technological processes. In the qualitative assessment of the ability of substances to form a homogeneous system, that is, to assess the compatibility of the hydrocarbon plasticizers and carbon nanomaterials under consideration, the presence of identical functional groups or structural elements in the molecules of these substances is taken into account. The phase compositions of hydrocarbon plasticizers, carbon nanotubes and divinyl styrene thermoplastic elastomers are complex, and molecules in different phase states exhibit different mixing behavior. Therefore, to predict the compatibility of the considered hydrocarbon plasticizers and the possibility of optimizing the experiment, we consider the Traxler dispersion coefficient [31], which takes into account the ratio between the sum of the concentrations of resins and aromatic hydrocarbons and the sum of the concentrations of asphaltenes and paraffin naphthenic hydrocarbons:

$$K_D = \frac{Ah+R}{PN+As}, \quad (1)$$

where K_D – Traxler dispersion coefficient, A_h – content of aromatic hydrocarbons, R – content of resins, PN – content of paraffin naphthenic hydrocarbons, A_s – asphaltenes content. It is obvious that it is possible to ensure uniformity of distribution in volume and high dispersion rate of primary nanomaterials in bitumen in components having relatively low viscosity and molecular weight. Such bitumen components include aromatic hydrocarbons [31]. It follows that bitumen for modification should be characterized by a high Traxler dispersion coefficient, and when choosing a plasticizer, it is necessary to give priority to plasticizers with a high content of aromatic fractions and resins.

2 Material and method research

2.1 Research materials

The following materials were considered as the investigated hydrocarbon plasticizers:

1) Industrial oil of the I40 A brand (I-40 SN 300), produced by Oil Coal LLC, Moscow, Russia which a low-viscosity liquid consisting of a complex mixture of hydrocarbons;

2) Extract of selective oil purification (ESOP), Lukoil-Perm oil refining LC, Perm, Russia. It is obtained at selective oil purification plants with phenolic purification of distillate and residual oil fractions;

3) III Vacuum shoulder strap (III VSS) manufactured by LLC Lukoil-Nizhegorodnefteorgsintez, Nizhny Novgorod, Russia. It is a product of the primary distillation of oil, which a mixture of liquid hydrocarbons.

The studied carbon primary nanomaterials (CPNM) were multi-walled carbon nanotubes (MWCNT) of the Taunit-M series, manufactured by Nanotech Center LLC, Tambov, Russia. They are quasi-one-dimensional nanoscale, filamentous formations of polycrystalline graphite of predominantly cylindrical shape with an internal channel. The outer diameter is in the range from 10 to 30 nm, the length is more than 2 microns, and the

bulk density is in the range from 0.025 to 0.06.

As a polymer, a polymer was considered, which is styrene-butadiene-styrene (SBS), divinyl styrene thermoplastic with a linear structure SBS 30L-01, corresponding to TU 38.40327-98, manufactured by JSC Voronezh synthesis of rubber, Voronezh, Russia.

Bitumen petroleum of the road brand BND 100/130, produced by Lukoil Nizhny Novgorod Oil Refinery LLC, Nizhny Novgorod, Russia, was considered as a bitumen binder. Bitumen was examined for compliance with the requirements of GOST 33133-14. The results of laboratory tests of the physical and mechanical properties of bitumen are presented in Table 1.

Table 1. Physical and mechanical characteristics of bitumen petroleum of the road brand BND 100-130.

Name of indicators	Russian state standard GOST R 33133	Actual indicators
Needle penetration depth, 0.1 mm, at temperature 25 °C	101–130	112
Softening temperature by ring and ball, °C	no less 45	47
Ductility, cm at temperature 0°C	no less 4,0	5,6
Fragility temperature, °C	no more -20	-20
Flash point, °C	no less 230	248
Change in the mass of the sample after aging, %	no more 0,7	-
Change in the softening temperature of the sample after aging, %	no less 7	4

2.2 Research methods

To calculate the compatibility parameter (formula 1), the group composition was determined for all the hydrocarbon plasticizers under consideration. The determination was carried out by the method of liquid adsorption chromatography with gradient displacement at the laboratory installation "Gradient M". The "Gradient M" setting is shown in Figure 1.



Fig. 1. Installation "Gradient M".

The principle of operation of Gradient – M is the separation of the analyzed product in a chromatographic column by a flow of a mobile phase which consisting of a mixture of solvents selected for a specific case of separation, transfer of the eluent in the form of a film to the transporting chain, removal of the components of the mobile phase in the evaporator, thermal oxidative destruction of the separated components of the analyte in the oxidizing cell and detection of the resulting carbon dioxide thermal conductivity detector. The katharometer compares the thermal conductivity of clean air and mixtures of air with

carbon dioxide. This difference in thermal conductivity leads to an imbalance of the equilibrium bridge of the detector. The recording of detector signals on the monitor screen is a chromatogram, and each group of the mixture corresponds to a certain peak.

The influence of the molecular weight of hydrocarbon plasticizers and the concentration of carbon primary nanomaterials in the studied systems on the dispersing ability of the medium was determined by the dispersion index of particles of multi-walled carbon nanotubes in the studied hydrocarbon plasticizers. Sampling to determine the average reduced diameter of multi-walled carbon nanotubes was carried out after ultrasonic dispersion by means of an immersion type disperser Vibrocell 750, in three different layers and at least three samples were taken from each layer using a calibrated dividing funnel.

The dispersion of particles of multi-walled carbon nanotubes in the volume of hydrocarbon plasticizers was determined using the laser diffraction method in the studied particle size range from 0.0008 to 6.5 microns on the Zetatract laser analyzer device of Microtrac Inc., in which a laser diode with a wavelength of 780 nm is used as a source of coherent monochromatic radiation.

The influence of the molecular weight of hydrocarbon plasticizers and the concentration of carbon primary nanomaterials in solution on the stabilizing effect of the medium was determined by determining the dispersion in the "multi-walled carbon nanotubes - hydrocarbon plasticizer" system after 6 and 9 months.

The methodology for the preparation of polymer nanomodified binder (PNB) is as follows. Bitumen is heated in a container with an airtight lid to an operating temperature of 150-160 ° C. Next, a mixer and a sensor for monitoring the heat supply are immersed in the container. The mixer is switched on at a speed of 100-300 rpm and the dispersed system "hydrocarbon plasticizer-carbon nanotubes" and polymer are introduced within 3-10 minutes. The preparation of the dispersed system "hydrocarbon plasticizer-carbon nanotubes" was carried out using an immersion ultrasonic dispersant until a homogeneous state was reached. The container with PNB B is hermetically sealed, mixing is carried out until the polymer is homogenized in the volume of bitumen. Then the polymer-bitumen binder is placed in a drying cabinet and stabilized at a temperature of 135 ° C.

The rational content of polymer and plasticizer in polymer-bitumen binder was previously selected. The selection was carried out according to the principle of the minimum required content of polymer and plasticizer necessary to achieve properties that meet the requirements of regulatory documents. The compositions of PNB binders are presented in Table 2.

Table 2. Compositions of polymer nanomodified binders.

Compositions	The name of the components of the NPMB, the content %					
	BND100/130	SBS 30L-01	OI I-40A	ESOP	III VSS	MWCNM Taunit-M
1	100	3.2	2.3	—	—	—
2	100	3.2	2.3	—	—	0.001
3	100	3.2	2.3	—	—	0.005
4	100	3.2	—	1.8	—	—
5	100	3.2	—	1.8	—	0.001
6	100	3.2	—	1.8	—	0.005
7	100	3.2	—	—	2.0	—
8	100	3.2	—	—	2.0	0.001
9	100	3.2	—	—	2.0	0.005

The quality of the obtained polymer nanomodified binders prepared with various plasticizers (Table 2) was evaluated by the following quality indicators:

- the structural stability of the PNB was evaluated by the shear stability $G^*/\sin \delta$ using a

dynamic shear rheometer DSR, operating on the principle of adjustable shear deformation in order to measure the properties of fluidity. The shear stability was determined using the geometry (two disks), where the diameter of the pad is 25 mm. On the dynamic rheometer, the test temperature was 82 oC. At least 3 samples were prepared and tested for each percentage of the modifier;

- physico-mechanical properties were evaluated by the needle penetration depth at temperatures of 25 oC and 0 oC, softening temperature by ring and ball (heat resistance) (according to Russian state standard GOST R 52056-2003, GOST R 58400.1-2019 and GOST R 58400.2-2019);
- destruction was assessed by the tendency of the nanomodified binder to aging;
- resistance to thermo-oxidative aging processes of PNB, it is planned to evaluate by changing the softening temperature and mass after warming up samples of nanomodified bitumen binders in a thin layer using the TFOT ("Thin-Film Oven") method. Aging is planned to be carried out at a temperature of 163 ° C, for 5 hours, this method allows you to simulate the actual process of thermo-oxidative aging occurring during the preparation of asphalt concrete mixture.

3 Result and discussion

Based on the results of the analysis of chromatograms and the obtained peaks, the group compositions of hydrocarbon plasticizers were determined and the Traxler coefficient was calculated (Table 3).

Table 3. Group composition of the studied hydrocarbon plasticizers and Traxler coefficient.

Name of components	OI I-40A	ESOP	III VSS
Paraffin - naphthenic hydrocarbons	68.3	11.55	34.21
Monocyclic aromatic hydrocarbons	7.5	–	–
Bicyclic aromatic hydrocarbons	19.2	–	–
Light aromatic hydrocarbons	–	15.90	16.20
Medium aromatic hydrocarbons	–	16.50	11.5
Heavy aromatic hydrocarbons	–	37.55	25.03
Resins (total quantity)	5.0	16.20	10.53
Asphaltenes	–	2.30	2.53
Traxler coefficient			
	0.46	6.22	1.72

Analysis of the data obtained (Table 3) shows that the highest value of the Traxler dispersion coefficient is characterized by an ESOP, which characterizes it as a plasticizer having high compatibility with carbon materials and polymers. So, additionally comparing the data on the Traxler coefficient and the selected compositions of polymer modified binders (Table 2), it can be noted that it is the ESOP plasticizer that is characterized by the lowest rational content to achieve properties corresponding to regulatory documents. Therefore, it can be concluded that with the help of this coefficient, it is possible to pre-select the most preferred plasticizer from a large sample, significantly reducing the number of experiments.

Nanomodification of bulk materials depends directly on the degree of dispersion and uniform volume distribution of multi-walled carbon nanotubes both in the carrier medium and in the modified composite matrix. Ultrasonic dispersion was considered for the dispersion and distribution of nanomaterials. The results of the effect of ultrasonic dispersion on the average reduced diameter of multi-walled carbon nanotubes "Taunit" are presented in Table 4-6. When calculating the average reduced diameter, the true density of the MWCNT was taken into account, which was equal to 1900 kg/m3. To determine the

degree of dispersion of the obtained data based on the results of the study of the effect of ultrasonic dispersion on the ability to achieve the nanoscale parameter of the MWCNT and the uniformity of the distribution of nanoparticles in the volume of the studied hydrocarbon plasticizers, the average value of the reduced diameter the standard deviation and the coefficient of variation were calculated.

Table 4. Effects of ultrasonic dispersion on the parameters of the dispersion and uniformity of the distribution of MWCNT Taunite-M (nm) in a system with OI I-40A.

USD time, min	Concentration of MWCNT Tounit-M,%								
	0.0005			0.005			0.05		
	D_{av} , nm	σ , nm	v , %	D_{av} , nm	σ , nm	v , %	D_{av} , nm	σ , nm	v , %
1	498	26.5	5.3	576	37.9	6.6	741	91.6	12.4
2	86	3.4	4.0	90	4.9	5.5	106	31.7	29.8
3	62	0.6	0.9	87	3.1	3.5	114	25.3	22.1
4	73	2.1	2.8	77	2.4	3.1	97	19.5	20.1
5	74	4.8	6.4	72	0.6	0.8	88	17.6	19.9
6	82	7.7	9.4	86	5.6	6.5	106	15.6	14.7
8	92	6.5	7.0	131	6.5	5.0	145	28.3	19.5

Note: D_{av} – average reduced diameter of MWCNT aggregates; σ – standard deviation; v – coefficient of variation.

Table 5. Effect of ultrasonic dispersion on the parameters of the dispersion and uniformity of the distribution of MWCNT Taunite-M (nm) in a system with ESOP.

USD time, min	Concentration of MWCNT Tounit-M,%								
	0.0005			0.005			0.05		
	D_{av} , nm	σ , nm	v , %	D_{av} , nm	σ , nm	v , %	D_{av} , nm	σ , nm	v , %
1	94	3.1	3.2	97	3.7	3.8	102	4.6	4.5
2	11	0.3	2.4	24	1.6	6.3	46	2.1	4.6
3	15	1.5	9.5	11	0.4	3.3	22	1.6	7.1
4	23	2.1	8.9	37	1.4	3.8	12	0.2	2.2
5	35	2.6	7.2	54	3.4	6.2	44	4.6	10.2
6	44	3.4	7.7	64	7.2	6.5	73	4.7	6.4
8	64	4.2	6.5	75	4.9	6.5	96	5.3	5.5

Table 6. Influence of ultrasonic dispersion on the parameters of dispersion and uniformity of the distribution of MWCNT Taunite-M (nm) in a system with III VSS.

USD time, min	Concentration of MWCNT Tounit-M,%								
	0.0005			0.005			0.05		
	D_{av} , nm	σ , nm	v , %	D_{av} , nm	σ , nm	v , %	D_{av} , nm	σ , nm	v , %
1	75	3.5	4.5	84	2.3	2.7	98	8.7	8.9
2	16	0.3	2.1	35	3.2	9.1	86	8.8	10.2
3	24	2.9	12.2	13	0.4	2.9	82	11.2	13.7
4	35	3.0	8.7	27	3.7	13.6	73	15.5	21.2
5	37	2.7	7.3	44	3.4	7.9	71	9.7	13.7
6	47	4.7	9.9	54	3.7	6.8	63	9.5	15.0
8	44	2.1	4.7	55	1.7	3.1	66	15.3	23.2

So, it was found that:

- for all the studied systems "MWCNT – hydrocarbon plasticizer", the minimum average reduced diameter of aggregates for different concentrations of Taunite-M is achieved with different duration of ultrasonic dispersion;
- in a system with industrial brand OI I-40A oil for a concentration of Taunite-M 0.0005%, the nanoscale parameter of the average reduced diameter equal to 62 nm is achieved with a duration of 3 minutes, while the coefficient of variation is less than 1%,

with a concentration of Taunite-M 0.005%, the average reduced diameter equal to 72 nm is reached after 5 minutes of ultrasound, the coefficient of variation is also less than 1%, and with an increase in the concentration of Taunite-M to 0.05%, it was not possible to achieve uniformity of distribution (coefficient of variation > 12%);

– in a system with a ESOP for a concentration of Taunite-M 0.0005%, the average reduced diameter of aggregates equal to 11 nm is reached after 2 minutes of ultrasound (coefficient of variation less than 3%), at a concentration of Taunite-M 0.005%, the average reduced diameter of aggregates equal to 11 nm is reached after 3 minutes of ultrasound (coefficient variations of less than 4%), and at a concentration of Taunite-M 0.05%, the average reduced diameter of 11 nm is reached after 4 minutes of ultrasound. At the same time, the coefficient of variation is less than 3 %;

– in a system with a III VSS range for a concentration of Taunite-M 0.0005%, the average reduced diameter of aggregates equal to 16 nm is reached after 2 minutes of ultrasound (coefficient of variation less than 3%), at a concentration of Taunite-M 0.005%, the average reduced diameter of aggregates equal to 13 nm is reached after 3 minutes of ultrasound (coefficient of variation less than 4%), with a concentration of 0.05% Taunite-M, it was not possible to achieve uniformity of distribution (coefficient of variation of more than 8%).

The effect of the molecular weight of the studied hydrocarbon plasticizers on the dispersing ability of the MWCNT particles is presented in Table 7.

Table 7. The effect of the molecular weight of the studied hydrocarbon plasticizers on the dispersing ability of the particles of MWCNT.

Name of the hydrocarbon plasticizer	Molecular weight	Concentration of Taunite-M,%	The average value of the reduced Dav, nm	Duration of the ultrasound, min
OI I-40A	2950	0.0005	62	3
		0.005	72	5
ESOP	3100	0.0005	11	2
		0.005	11	3
		0.05	11	4
III VSS	3600	0.0005	16	2
		0.005	13	3

According to the results of data analysis (Table 7), it was found that there was no influence of molecular weight on the dispersing ability of the MWCNT Taunite-M particles.

The influence of the molecular weight of hydrocarbon plasticizers and the concentration of MWCNT in solution on the stabilizing effect of the medium was determined by determining the dispersion in the "MWCNT – hydrocarbon plasticizer" system after 6 and 9 months (Tables 8 and 9).

Only those samples of systems in which a nanoscale parameter and a uniform distribution of multi-walled carbon nanotubes in the volume of a hydrocarbon plasticizer were previously achieved were studied.

Table 8. Effect of the molecular weight of hydrocarbon plasticizers and the concentration of carbon primary nanomaterials in the system on the stabilizing effect of the medium after 6 months of storage.

Name of the hydrocarbon plasticizer (molecular weight)	concentration of MCWNT Taunite-M, %								
	0.0005			0.005			0.05		
	sample layers								
	L	M	U	L	M	U	L	M	U
OI I-40A (2950)	95	97	104	132, 3	149	103	—	—	—
	91	74	75	173, 5	111	119	—	—	—
	74	101	82	132	99	112	—	—	—
Standard deviation	13.9			19.4			—		
Coefficient of variation	17.7			19.2			—		
ESOP (3100)	13	12	12	12	14	13	13	14	12
	12	12	12	13	13	13	13	13	12
	12	12	12	12	13	12	13	14	12
Standard deviation	0.3			0.4			0.3		
Coefficient of variation	2.4			2.8			2.0		
III VSS (3600)	17	18	17	14	15	15	—	—	—
	17	17	16	15	15	15	—	—	—
	16	17	16	15	15	15	—	—	—
Standard deviation	0.4			0.4			—		
Coefficient of variation	2.1			2.5			—		

Note: L – lower; M – middle; U – upper.

Table 9. Effect of the molecular weight of hydrocarbon plasticizers and the concentration of carbon primary nanomaterials in the system on the stabilizing effect of the medium after 9 months of storage.

Name of the hydrocarbon plasticizer (molecular weight)	concentration of MCWNT Taunite-M, %								
	0.0005			0.005			0.05		
	sample layers								
	L	M	U	L	M	U	L	M	U
ESOP (3100)	14	13	14	13	15	14	16	17	16
	14	14	14	14	15	14	16	16	15
	13	14	13	14	14	14	17	17	15
Standard deviation	0.3			0.4			0.5		
Coefficient of variation	2.2			2.6			3.0		
III VSS (3600)	19	20	19	16	17	17	—	—	—
	19	19	19	17	16	16	—	—	—
	19	19	18	16	17	17	—	—	—
Standard deviation	0.4			0.4			—		
Coefficient of variation	2.1			2.5			—		

It was found that for a system based on Industrial Oil brand I-40A visible particle deposition is observed during the 7th month of storage, which indicates the instability of the system. The most promising hydrocarbon plasticizer from the point of view of the stability of the dispersed system is the ESOP. In the entire percentage range of the Taunite-M particle content (from 0.0005 to 0.05%), this system is characterized by stability and stability for 9 months. This opens up prospects for further research on the possibility of creating highly concentrated nanomodified granules based on it, as well as obtaining more stable and resistant to the processes of destruction of polymer-bitumen binders. With a nanoparticle content of 0.02%, it was impossible to obtain stable dispersed systems with OI I-40A and III VSS in further studies, this percentage was not considered.

To establish the maximum possible critical operating temperature of nanomodified binders, the shear ($G^*/\sin \delta$) was determined, at 10 rad/s, at different temperatures, the results are shown in Figure 2.

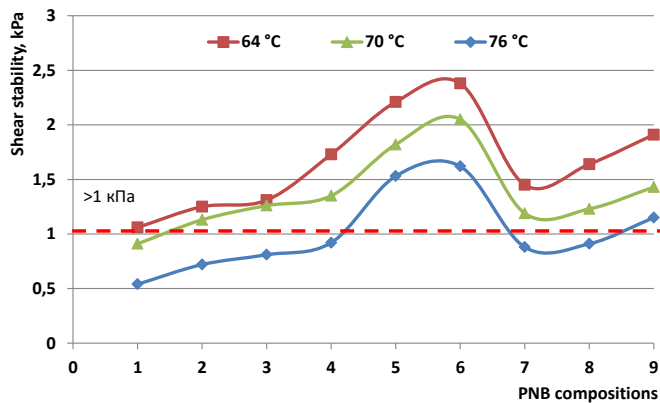


Fig. 2. Influence of the component composition of PNB and the test temperature on shear stability.

As the analysis of Figure 2 shows, the introduction of a nanomodifier (regardless of the content) into polymer modified binders prepared with industrial oil (No. 2 and No. 3) makes it possible to increase the operating temperature of the initial binder by one brand, which is 70 oC. The introduction of Taunite-M (regardless of the content) into polymer modified binders prepared with ESOP (compositions No. 5 and No. 6) allows increasing the operating temperature of the control binder by one brand, which is 76 oC. The introduction of 0.001% Taunite-M into a polymer modified binder prepared with a III VSS does not provide an increase in the operating temperature of the binder, whereas the introduction of 0.005% Taunite-M provides an increase in the operating temperature of the control binder by one grade, which is 76 oC. So, it is established that the maximum possible critical operating temperatures of the investigated binders correspond to the data presented in Table 10.

Table 10. Maximum possible critical operating temperatures of PNB.

The name of the indicator	Number of composition and component composition of binders, %		
	(№1) OI I-40A	(№4) ESOP	(№7) III VSS
Maximum possible critical operating temperature, oC	64	70	70
	(№3) OI I-40A (+0.005% Taunit-M)	(№5) ESOP (+0.001% Taunit-M)	(№9) III VSS (+0.005% Taunit-M)
	70	76	76

Analyzing the data on the structural stability of modified binders (Figure 3, Table 10), it can be concluded that the use of a compatible plasticizer (composition No. 5) makes it

possible to fully reveal the structuring potential of multi-walled carbon nanotubes, which makes it possible to reduce the content of the nanomodifier without deterioration of properties. The results of the influence of the component composition of modified binders on the indicators of physical and mechanical properties are presented in Table 11.

Table 11. Physical and mechanical properties of the polymer nanomodified binders.

The name of the indicator	The composition the PNB and the values of quality indicators								
	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9
Needle penetration depth, 0.1 mm, at temperature 25 °C	85	83	82	80	77	75	82	79	77
Needle penetration depth, 0.1 mm, at temperature 0 °C	32	35	34	36	35	36	33	34	35
Softening temperature by ring and ball, °C	64	71	73	75	79	80	71	74	78
Softening points after RTFO aging	70	75	77	79	79.9	80.9	75	77	79.8
Δ Softening points after RTFO aging	6	4	4	3	0.9	0.9	4	3	1.8

The analysis of the data indicators of physical and mechanical properties presented in Table 11 confirms the previously established patterns. So, the better results of polymer nanomodified binders correspond to compositions No. 5 and No. 6. The introduction of 0.001% MWCNT into the binder with ESOP allows for structuring of the binder, which slows down the aging process by 3 times. The introduction of 0.005% MWCNT into the binder with the III VSS (composition No. 9) allows to slow down the aging process by more than 2 times. The introduction of 0.005% MWCNT into the binder with OI I-40A (composition No. 3) also makes it possible to slow down the aging process, but not so intensively – by 34%.

4 Conclusion

It was found that the highest value of the Traxler dispersion coefficient is characterized by the ESOP which characterizes it as a plasticizer having high compatibility with carbon materials and polymers. It is also established that the ESOP is characterized by the lowest content to achieve properties corresponding to regulatory documents. Therefore, it is natural to conclude that with the help of this coefficient, it is possible to pre-select the most preferred plasticizer from a large sample, significantly reducing the number of experiments.

It is established that for all the studied systems "MWCNT – hydrocarbon plasticizer" the minimum parameter of the average reduced diameter for different concentrations of Taunite-M is achieved with different duration of ultrasonic dispersion. So, in a system with OI I-40A for a concentration of Taunite-M 0.0005%, the minimum diameter equal to 62 nm is reached after 3 minutes of ultrasound (coefficient of variation less than 1%), with a concentration of Taunite-M 0.005%, the minimum diameter of aggregates equal to 72 nm is reached after 5 minutes of ultrasound (coefficient of variation less than 1%), with a concentration of 0.05% Taunite-M it was not possible to achieve uniformity of distribution (coefficient of variation of more than 12%). In a system with a ESOP for a concentration of Taunite-M 0.0005%, the average reduced diameter of aggregates equal to 11 nm is reached after 2 minutes of ultrasound (coefficient of variation less than 3%), at a concentration of Taunite-M 0.005%, the average reduced diameter of aggregates equal to 11 nm is reached after 3 minutes of ultrasound (coefficient of variation less than 4%), and at a concentration

of Taunite-M 0.05%, the average reduced diameter of 11 nm is reached after 4 minutes of ultrasound. At the same time, the coefficient of variation is less than 3%. In a system with III VSS for a concentration of Taunite-M 0.0005%, the reduced average diameter of aggregates equal to 16 nm is reached after 2 minutes of ultrasound (coefficient of variation less than 3%), with a concentration of Taunite-M 0.005%, the reduced average diameter of aggregates equal to 13 nm is reached after 3 minutes of ultrasound (coefficient of variation less than 4%), with a concentration of 0.05% Taunite-M, it was not possible to achieve uniformity of distribution (coefficient of variation of more than 8%).

It has been established that the molecular weight of hydrocarbon plasticizers has no effect on their dispersing ability of Taunite-M particles, as well as the absence of a direct pattern in influencing the stability during storage of dispersed systems. The most promising hydrocarbon plasticizer from the position of ensuring high stability of the dispersed system is ESOP. In the entire percentage range of the Taunite-M particle content (from 0.0005 to 0.05%), this system is characterized by stability and stability for 9 months. This opens up prospects for further research on the possibility of creating highly concentrated nanomodified granules based on it, as well as obtaining more stable and resistant to the processes of destruction of polymer nanomodified binders.

According to the structural stability data of polymer nanomodified binders, it was found that the use of a compatible plasticizer ESOP (composition No. 5) makes it possible to fully reveal the structuring potential of multi-walled carbon nanotubes, which makes it possible to reduce the content of the nanomodifier with simultaneous improvement of properties.

It was found that the introduction of 0.001% MWCNT into the binder with a residual extract allows structuring of the binder, slowing down the aging process by 3 times. The introduction of 0.005% MWCNT into the binder with the III VSS (composition No. 9) allows to slow down the aging process by more than 2 times. The introduction of 0.005% MWCNT into the binder with OI I-40A (composition No. 3) also makes it possible to slow down the aging process, but not so intensively – only by 34%.

Acknowledgements

Financial support for this work was obtained from Russian Science Foundation contract numbers: 21-79-00191, <https://rscf.ru/en/project/21-79-00191/>.

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