Nanomodified Polymer-Bitumen Binders

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Abstract. A modification of petroleum bitumen for road building was carried out by devulcanizing rubber crumb and adding modified dispersion, consisting of single-walled carbon nanotubes (SWCNT), distributed in industrial oil (I-20A). To solve the problem of distribution of nanotubes in industrial oil I-20A it is necessary to «break» their aggregates using ultrasound [26–28]. The SWCNTs distribution was observed using a HoribaLA-950 laser analyzer and a KFK-3 photoelectric photometer for optical density evaluating. Softening point, penetration index (PI), penetration at 25 °C (P25), ductility at 25 °C (D25) and elasticity at 25 °C (E25) were respectively determined to GOST 32054-2013, GOST 33134-2014, GOST 33136-2014, GOST 33138-2014, GOST EN 13398-2013 (Russian standards). With the introduction of nanotubes, the effect of the dispersed phase on the properties decreases and the presence of nanotubes in dispersion, when introduced after devulcanization, does not give a plasticizing effect. But it simultaneously increases both ductility and elasticity, which is rarely observed. The introduction of nanotubes before devulcanization plasticizes the binder by reducing the thermal distillation of the oil during devulcanization or by the plasticizing effect of nanotubes.

Keywords: Bitumen · Bitumenpolymer binder · Nanomodified · Nano · Bitumen modifications

1 Introduction

It is generally accepted that physical or chemical modification is one of the most effective ways to obtain or improve the properties of almost any composite building material [1–4].

Modifying petroleum bitumen with polymers allows, as it is known from [5–7], eliminating a number of disadvantages associated with binders. The most important of them are a narrow temperature range of plasticity, insufficient resistance to atmospheric aging, and low elasticity [8–10]. However, the high cost of the polymer leads to a strong increase in the cost of the final product.

Earlier [11], a bitumen-polymer composition was developed, obtained by devulcanization of rubber crumb in a bitumen environment, which features a high range of properties and is able to solve the problem of high cost of bitumen-polymer binders (BPB) and environmental pollution. The modification technology was as follows: rubber crumb and a devulcanizing agent (DA) were introduced into the heated petroleum bitumen with constant stirring. The composition, however, was characterized by low elongation. These disadvantages are common to all BPBs [12, 13], which nevertheless

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limits their application. These disadvantages can be eliminated by introducing plasticizers, but their use leads to a decrease in the softening point and an increase in the tendency to aging due to thermal distillation [14–16]. Moreover, the paradoxical effect of reducing the viscosity of binders (and couplers) when introducing carbon nanomaterials, e.g., in bitumen, is known [17–19].

2 Materials and Methods

To achieve a uniform distribution of nanotubes in a bitumen-polymer binder, it is also necessary to use a plasticizer, but the total amount of it in the binder is much lower. We used I-20A industrial oil as a plasticizer.

It is known from literature [20–22] that when single-walled carbon nanotubes (SWCNT) are added to bitumen, the complex of the obtained properties is higher than when it is modified with multi-walled carbon nanotubes (MWCNT). SWCNTs are characterized by such factors as high strength of sp 2 C–C bonds, high packing density of atoms in graphenes, absence or low density of structural defects [23–25]. We used SWCNT by «Tubal», Novosibirsk. The characteristics of the used SWCNTs are presented in Table 1.

Table 1. Characteristics of Tuball TM (Batch number 73-21052015).

Parameters	Unit	Values	Assessment method
Carbon content	wt. %	92 ± 1	TGA, EDA
CNT content	wt. %	76 ± 1	TEM, TGA
Metallic impurities	wt. %	8 ± 1	EDA, TGA
Number of walls in CNT	units	1–2	TEM
Length	microns	>5	AFM
Outer average diameter of CNT	nm	1.4 ± 0.15	Raman spectroscopy, TEM
G/D ratio	units	161	Raman spectroscopy, 488 nm
Total specific surface	m^2/g	450	Adsorption of N_2 at 77K

Initially, CNTs were introduced into industrial oil, and then the binder was modified with the resulting dispersion. This dispersion, as well as the model system in the form of pure I-20A oil without SWCNTs, were introduced in two ways: either simultaneously with rubber crumb (RC), or after the devulcanization process into the finished bitumen-polymer binder. The optimal concentration of nanotubes in bitumen was considered $5{\cdot}10^{-5}$ ppm, according to [20]. The content of the plasticizer was calculated in such a way that the optimal concentration of nanotubes in the bitumen was achieved at a concentration of plasticizer of 2%, which corresponds to its usual content. The maximum plasticizer concentration was initially limited to four percent.

To solve the problem of distribution of nanotubes in industrial oil I-20A, it is necessary to «break» their aggregates using ultrasound [26–28]. The SWCNTs distribution was observed using a HoribaLA-950 laser analyzer and a KFK-3 photoelectric photometer for optical density evaluating. Softening point, penetration index (PI), penetration at 25 °C (P_{25}), ductility at 25 °C (D_{25}) and elasticity at 25 °C (E_{25}) were respectively determined to GOST 32054-2013, GOST 33134–2014, GOST 33136-2014, GOST 33138-2014, GOST EN 13398-2013 (Russian standards).

3 Results and Discussions

For clarity, the particle size distribution of the dispersion was determined up to (Fig. 1) and after (Fig. 2) sonication.

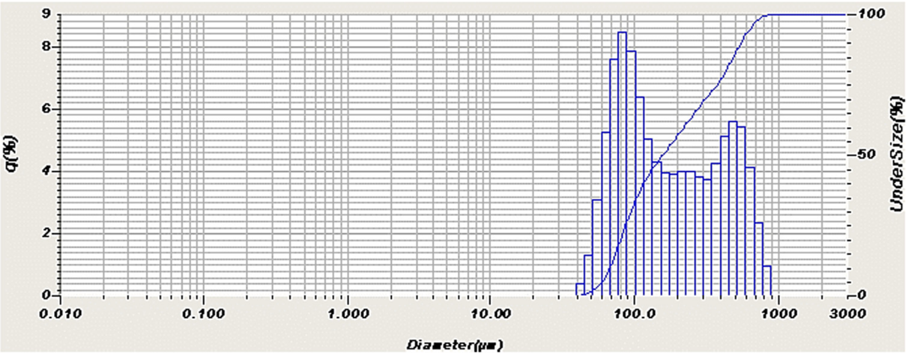

Fig. 1. Particle size before sonication.

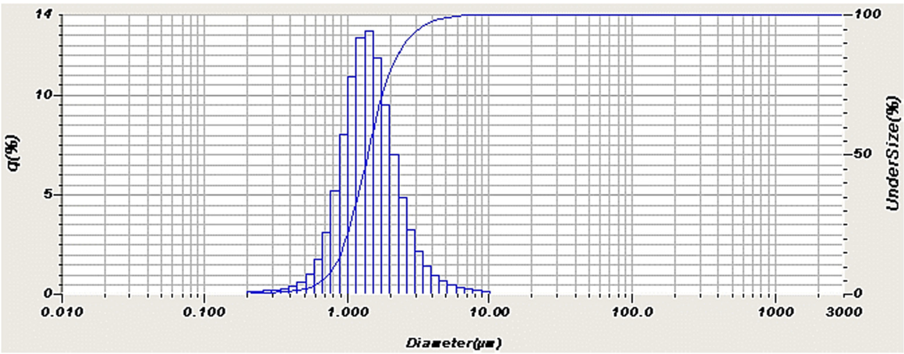

Fig. 2. Particle size after 10 min of sonication.

With dispersion, the histogram shifts to the left, which can be seen when comparing Fig. 1 and 2, i.e., the particle size after sonication became significantly smaller. The optimal dispersion time t was 10 min, since further ultrasonic exposure was not accompanied by a change in the histogram. Furthermore, the absolute particle size, according to the laser analyzer, does not reach the «nano» level, but it must be remembered that the device is designed to determine the size of spherical particles. It should also be noted that the Gaussian distribution in Fig. 2 indicates the presence of one dominant size in the initial SWCNT product, i.e., its purity.

Photoelectric photometer KFK-3 (photometer) is designed to measure the transmittance and optical density of transparent solutions and transparent solid samples [29, 30].

The principle of operation of the photometer is based on comparing the luminous flux F0, passed through the standard solution, in relation to which the measurement is carried out, and the luminous flux F, passed through the investigated solution. The photodetector converts light fluxes F0 and F into electrical signals U0, U and UT (UT signal when the receiver is not illuminated) which are processed by a microcomputer photometer and presented on the digital board as the transmittance (T) and optical density (D).

It was experimentally determined that the optimal wavelength for measuring optical density and transmittance is $\lambda = 430$ nm. Dispersion was carried out in an ultrasonic bath. Optical density was measured every 30 s. The increase in optical density with increasing time of ultrasonic treatment is shown in Fig. 3. The transmission ratio decreases rapidly with increasing optical density, and, as it is known, depends on it in the following way: T = 10-D. When the optical density is equal to 2, the transmittance becomes so low (0.01), that it ceases to be recorded by the photometer.

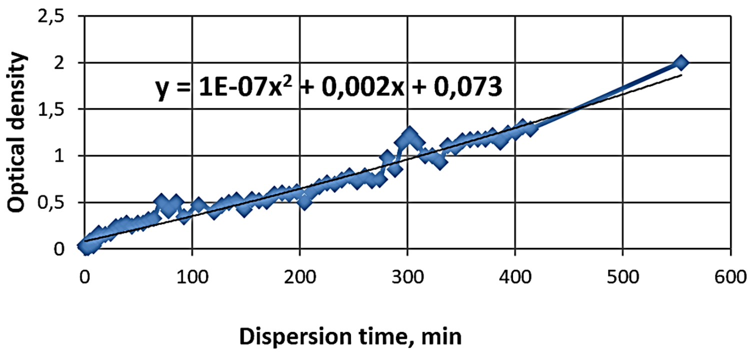

Fig. 3. A graph of optical density versus dispersion time.

Thus, according to the results of the data obtained using a Horiba LA-950 and a KFK-3 spectrophotometer, the optimal dispersion time required for the distribution of nanotubes in oil was accepted as $t = 10$ min.

Figure 4 shows the dependence of the softening point of the binder on the concentration of the modifying dispersion.

Comparing curves 3 and 4 it can be seen that the introduction of nanotubes induces the plasticization of the binder probably due to a decrease in the thermal distillation of the oil during devulcanization. A comparison of curves 1 and 2 shows that the presence of nanotubes in the dispersion, when introduced after devulcanization, has no effect. Curve 3 lies above curve 1, which indicates the volatilization of oil during devulcanization; however, curves 2 and 4 are close to each other, which again indicates that, in the presence of nanotubes, the oil either does not thermally distill during the devulcanization process, or thermal distillation is compensated by the plasticizing effect of the tubes. This effect is confirmed by penetration data (Fig. 5). In this case, the introduction of SWCNTs, regardless of the method of preparation of the binder, increases its hardness, which can be seen from a comparison of curves 1 and 2, as well as curves 3 and 4 in Fig. 5.

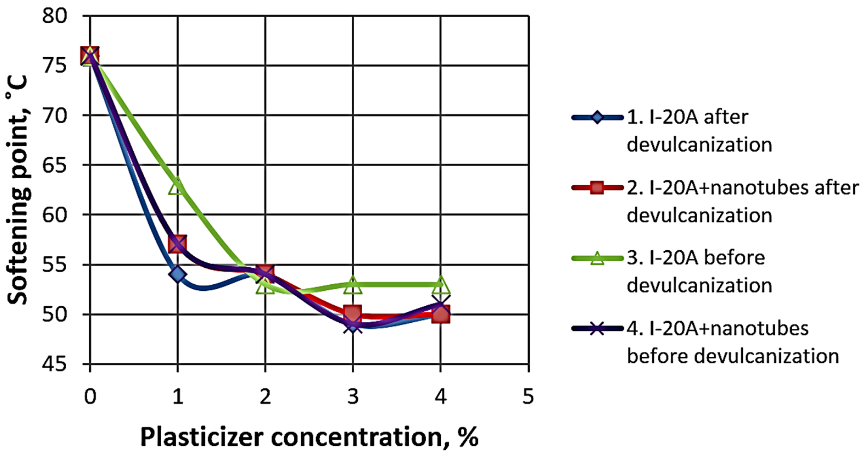

Fig. 4. Dependence of the softening point of the binder on the concentration of the dispersion.

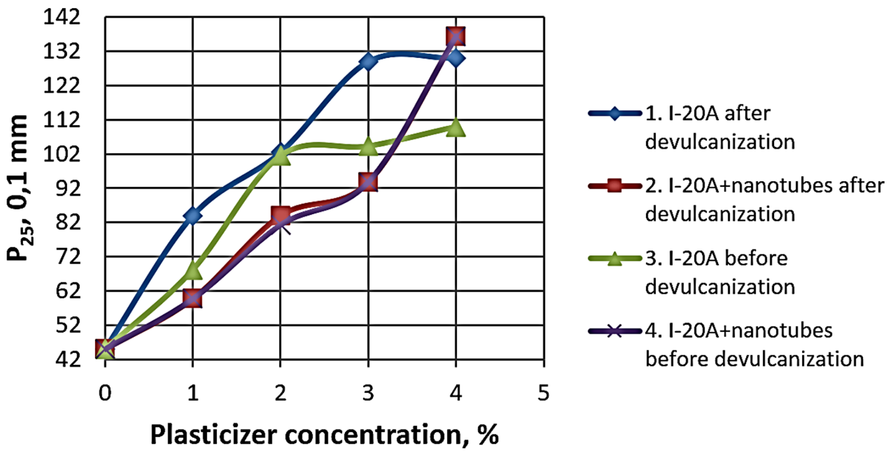

Fig. 5. Dependence of the binder penetration on the concentration of the modifying dispersion.

Figure 6 shows the dependence of the ductility of the binder on the concentration of the modifying dispersion. Noteworthy is the extremum with 3% of variance. It is obvious that the tubes significantly increase the extensibility of the binder. It is known [31–33] that the more bitumen deviates from the Newtonian flow, the less it is extensible. Put in other words, carbon nanotubes do not structure the binder, but, rather, bring the nature of its flow closer to the Newtonian one.

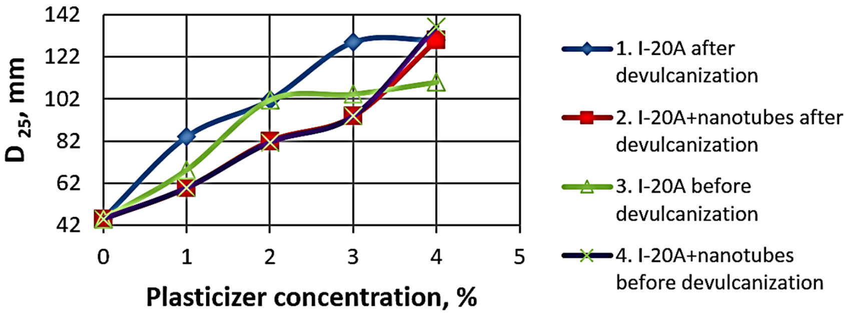

Fig. 6. Dependence of the ductility of the binder on the concentration of the modifying dispersion.

It should be noted that nanotubes introduced into the finished composition increase both ductility and elasticity simultaneously (curves 1 and 2 in Fig. 6 and 7), which is rarely observed. This effect does not appear after heat treatment of the binder during devulcanization, and the low elasticity of composites with SWCNTs (curves 3 and 4 in Fig. 7) is associated with an increase in the plasticity of the BPB [34, 35], reflected in the results of ductility.

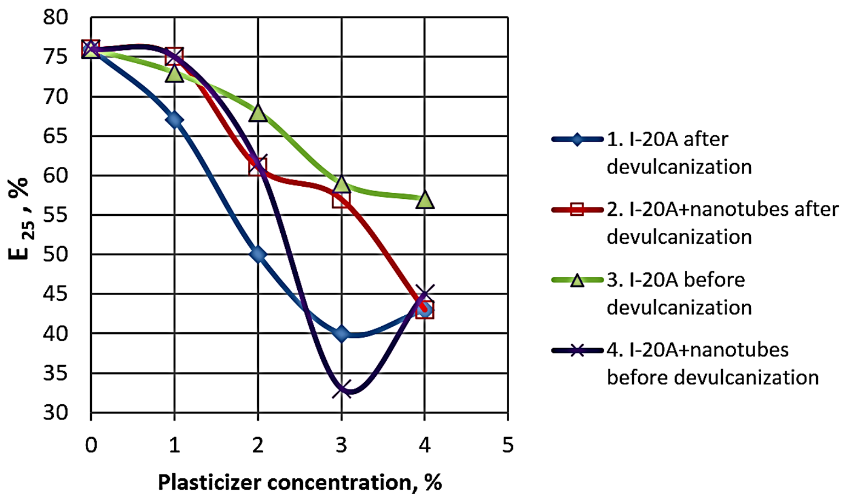

Fig. 7. Dependence of the elasticity of the binder on the concentration of the modifying dispersion.

Curves 2 and 4, characterizing binders with nanotubes, lie lower than curves 1 and 3 (Fig. 8), i.e., with the introduction of nanotubes, the degree of colloid of the binder decreases, that is the effect of the dispersed phase on the properties.

It should be noted that all developed binders have disadvantages typical for plasticized bitumen. However, the introduction of carbon nanotubes through a plasticizer makes it possible to evenly distribute them in the volume of the binder, and the above results allow us to see their effect on the properties of the composition.

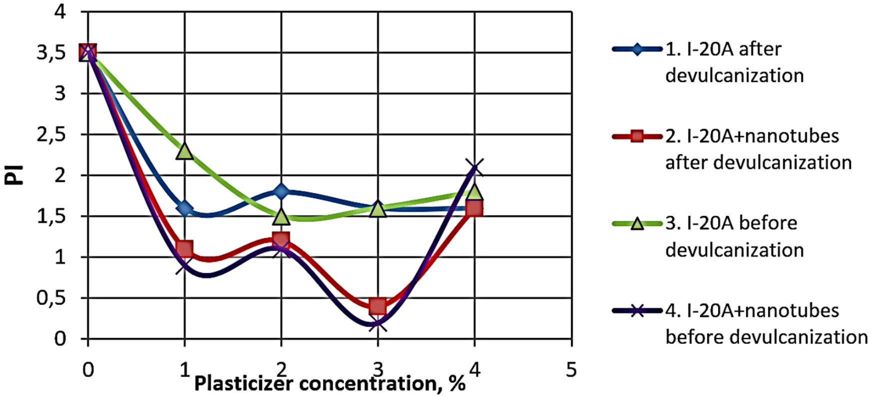

Fig. 8. Dependence of the bitumen penetration index on the SWCNT concentration.

4 Conclusion

1. The introduction of nanotubes before devulcanization plasticizes the binder by reducing the thermal distillation of the oil during devulcanization or by the plasticizing effect of nanotubes.
2. The presence of nanotubes in a dispersion, when introduced after devulcanization, does not give a plasticizing effect, but it simultaneously increases both ductility and elasticity, which is rarely observed.
3. With the introduction of nanotubes, the effect of the dispersed phase on the properties decreases.

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