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Improving the Quality of Materials for Highway Construction

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Abstract: The study is devoted to studying the possibility of improving the quality of asphalt concrete and cement concrete for road surfaces. We have shown the interaction which occurs between the components of mixed thermoplastic elastomer and matrix of petroleum bitumen for road building. We have proved a presence of a chemical reaction between mixed thermoplastic elastomer and a bitumen matrix on unsaturated C = C bonds with formation of a lightly crosslinked polymer within polymeric-bitumen binder. We have established that an introduction of polycarboxylate superplasticizers in cement concrete composition reduces chemical shrinkage and thereby increase its physical-mechanical characteristics.

Key words: Polymeric-bitumen binder, thermoplastic elastomer, IR spectroscopy, asphalt concrete, contraction, fine-grained concrete, strength

INTRODUCTION

Currently, cement concrete and asphalt concrete are equally used for construction of road pavements; each of them has its own advantages and disadvantages. The average term of road pavements service life in the United States is 26 years for slab concrete pavements and 16 years for asphalt concrete. Similar data are available for high-speed roads in Germany. Roadway replacement for asphalt concrete is needed on average after 18 years and for cement concrete after 26 years (Ushakov, 2016). To improve the durability of the materials, it is necessary to use modern methods of modification of concrete structures what will not only increase the strength characteristics but also the service life of road pavements.

The main component of asphalt concrete is bitumen. Modifying bitumen with polymers is recognized as the necessary technological method for producing high-performance building materials (Ouyang *et al*., 2005; Polacco *et al*., 2005). It was found that the most effective modifiers of bitumen on a complex of technological and operational properties are synthetic Thermoplastic Elastomers (TPE) (Fawcett and Nally, 2000; Makarov *et al*., 2014; Ayupov *et al*., 2015). However, a bitumen modifier the most commonly used among them is Divinistyrole Thermoplastic Elastomer (DST) having a number of disadvantages including poor resistance to climatic effects. In this regard, the first goal was set: to create a thermoplastic elastomer having advantages of the divinistyrole thermoplastic elastomer but without its disadvantages and having the utmost modifying effect.

The use of cement concrete as a material for road pavements requires a significant increase in its strength. An advantage of using high-strength fine-grained concretes is making high performance pavements. Features of fine-grained concrete are determined by the same factors as that of normal concrete. It is necessary to note also disadvantages of cement-sand concrete due to its structure which is characterized by: greater uniformity and fineness, a high content of cement rocks, the lack of hard stone skeleton, increased porosity and surface area of the solid phase. Upon that, increase in cement consumption leads to increased shrinkage and creep deformations.

It is therefore necessary to choose other ways to increase the strength taking into account the features of sand concrete. Well-known disadvantages of fine-grained concretes (high cement content and, therefore, significant shrinkage deformations and high cracking resistance) are eliminated by optimization of sand grading and effective use of chemical additives (Khozin *et al*., 2009).

It is known that the use of superplasticizers is technologically the simplest way of modifying heavy concrete including sand concrete. Selection of such additives in concrete technology is based on their performance depending on the type of cement and fillers (Plank and Hirsch, 2007; Krasinikova *et al*., 2014). With modern superplasticizers based on polycarboxylates a significant reduction in the water cement ratio is reached what increases not only the strength but also increases the durability of concrete. Therefore, the second objective

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was to increase the fine concrete strength by common use of effective superplasticizers and active mineral additives.

MATERIALS AND METHODS

Technique: Registration of IR spectra was carried out using a Frustrated Total Internal Reflection device (FTIR) Miracle ATR (ZnSe crystal) within the range of 4000-650 cm^{-1} in the FTIR spectrophotometer manufactured by company Perkin-Elmer, model Spectrum 65, under standard conditions of registration. Spectra were processed using the supplied software. The spectra were recorded at room temperature for bitumen samples in the form of viscous droplets applied directly to the crystal of the frustrated total internal reflection device. Spectra were recorded for samples of modifying agents in the form of granules pressed against the element of the frustrated total internal reflection device by a special holder, included in a device kit.

Research of cement systems contraction was conducted using the method of V.V. Nekrasov in a glass vessel at W/C = 0.5. If to measure not the external dimensions of samples as is carried out upon determination of swelling and shrinkage but the total volume of the system consisting of solid and liquid substances, a decrease in volume of the system is always observed. This total compression during the system (cement + water) curing is called contraction. Determination of the contraction can be performed in an ordinary glass jar with a rubber stopper through which a narrow part of the burette with 25-50 mL capacity and graduated in 0.1 mL is passed. Weigh of 350 g cement were mixed with 175 g water (W/C = 0.5) and after thorough mixing, the resulting paste in an amount of 450 g is introduced into the vessel through a glass funnel. For mixing cement freshly boiled (cooled) or distilled water should be taken.

Tapping the bottom of the vessel to the edge of a table, bring the paste into a compact state, after which the vessel was carefully (to avoid roiling of the cement paste) filled with water up to the plug level. In order to eliminate water evaporation from a burette several drops of mineral oil should be poured to its surface. Further readings should be made in the set time intervals. Up to 7 days age, it is recommended to make readings on the burette every day, then (up to 28 day age) in 2-3 days and then 1 time per week. When performing counts, it is necessary to introduce a correction for temperature changes to the level of the meniscus. Contraction is expressed in milliliters per gram of cement. Test of strength characteristics of concrete is performed according to standard normative techniques.

RESULTS AND DISCUSSION

Main part: Modification of bitumen with mixed thermoplastic elastomers was conducted when up-grading asphalt concrete. The mixed thermoplastic elastomer composition designed by us may include adhesive additive Azole which is a liquid composition of amidoamines and imidazoline and tall acids in a high boiling hydrocarbon solvent. Introduction of Azole gives flexibility to a modified bitumen, reduces its aging after heating, greatly increases the adhesion of bitumen with mineral material surface.

The aim of this study was to determine the nature of interactions that occur between the components of the mixed thermoplastic elastomer and the matrix of Petroleum Bitumen for Road Building (PBRB). Introduction of polymers in the capacity of modifiers leads to significant change in mechanical and rheological Properties of Polymeric-Bitumen Binders (PBB). IR spectroscopy has allowed studying the interaction of the mixed thermoplastic elastomer with bitumen of grade BND 60/90 used in road construction.

Figure 1 shows the difference spectrum between a polymeric-bitumen binder with a thermoplastic elastomer (4%) and the original bitumen 60/90 (curve 1). Figure 1 also shows the spectrum of the thermoplastic polymer itself (curve 2).

As you can see, the difference spectrum repeating range of mixed thermoplastic elastomer in the area of stretching and deformation vibrations of CH_2 and CH_3 groups, as well as in the area of C = O at 1740 cm^{-1} does not register bands of C = C bonds at 1665 cm^{-1}. This points to the fact that introduction of a thermoplastic elastomer in hot bitumen may disclose unsaturated vinyl groups with formation of a lightly crosslinked polymer within BND 60/90 matrix. Presumably, this process is catalyzed by sulfur compounds that are part of the bitumen. As is known, rubber substance vulcanization occurs using sulfur atoms to form sulfur bridges C-S-C. We were unable to identify vibrations band v (C-S) in the spectra of the modified compositions due to its low intensity and low content of thermoplastic elastomer in the composition of polymeric-bitumen binders (4%).

The adhesive additive Azole was introduced in the composition of a number of the studied mixed thermoplastic elastomers in the amount of 0.4% by weight of the polymeric-bitumen binders. Introduction of Azole in the mixed thermoplastic elastomer improves such process parameter as the mixing time of polymeric-bitumen binder. At a temperature of 165°C it is necessary to spend 2 h to obtain a homogeneous composition of the

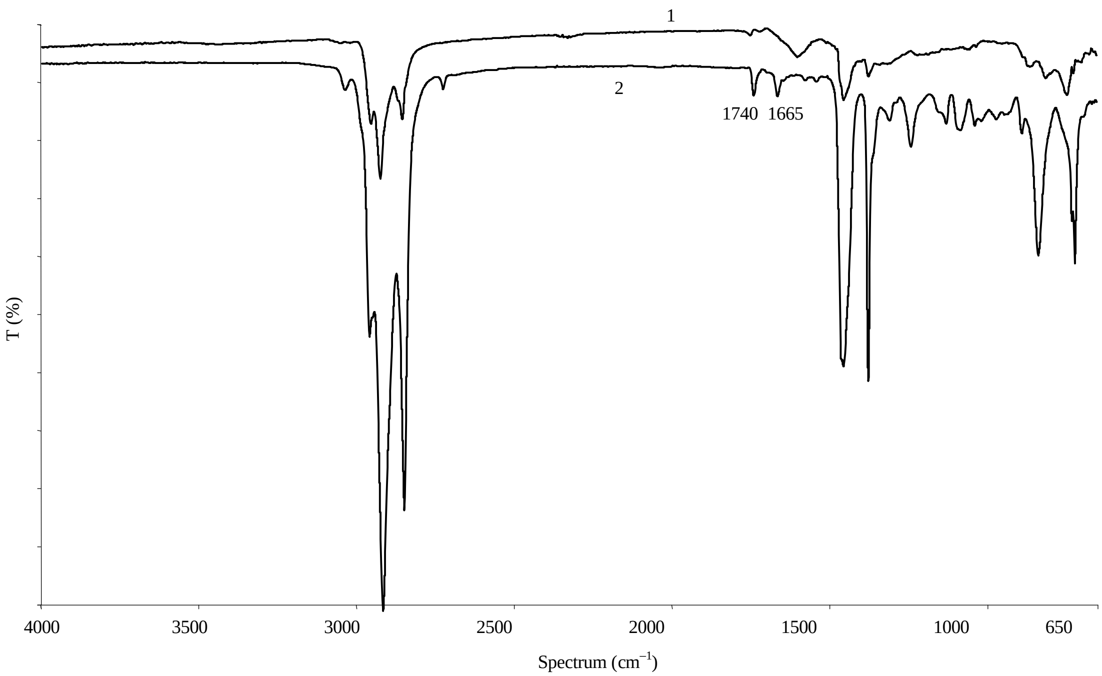

Fig. 1: The difference spectrum of the polymeric-bitumen binders with thermoplastic elastomer and BND 60/90 (curve 1) and IR spectrum of the thermoplastic elastomer (curve 2)

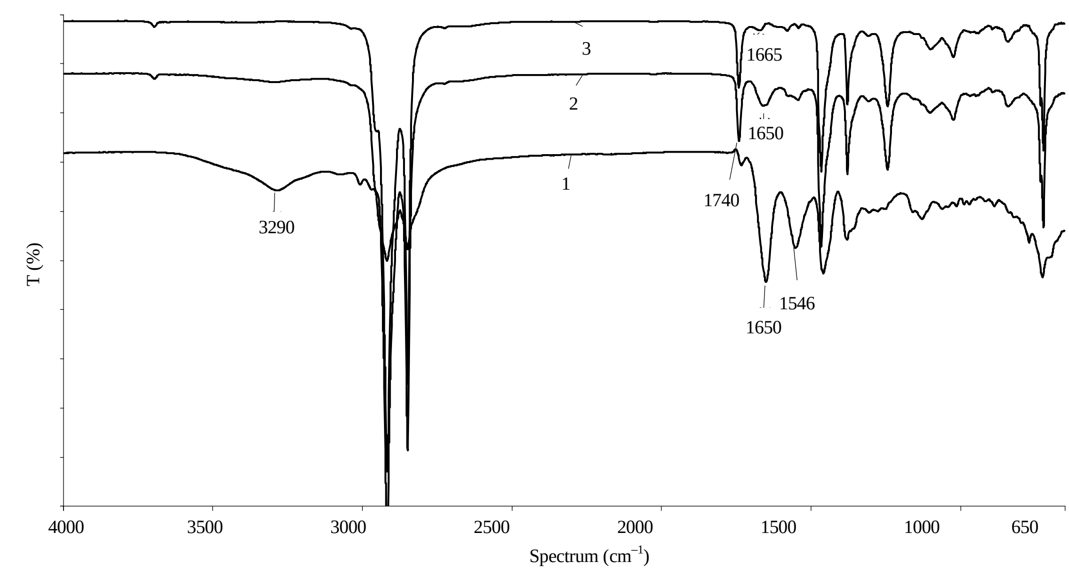

Fig. 2: IR spectra of Azole (curve 1), a thermoplastic elastomer + Azole composition (curve 2) and their difference spectrum (curve 3)

polymeric-bitumen binders in a dispersant what is 30% less than when using mixed thermoplastic elastomer without Azole (3 h).

The spectrum of a liquid Azole is shown in Fig. 2 (curve 1) which being a secondary amine is characterized by the presence of stretching (3290 cm^{-1} band) and deformation vibrations of N-H groups (1546 cm^{-1} band) and quite intense band of the bond C = N at 1650 cm^{-1} which is characteristic for imidazolines. This Fig. 2 (curve 2) shows the spectrum of a thermoplastic elastomer

Table 1: Physical and mechanical properties of stone mastic asphalt mixture SMA-15

Composition	Average density of stone-mastic asphalt (g/cm^3)	Water saturation (% by volume)	Compressive strength (Mpa)		Shear resistance		Cracking resistance at rupture (at 0°C)	Segregation resistance	Water resistance for prolonged water saturation K_w
			R_{20}	R_{50}	Internal friction coefficient	Shear adhesion at 50°C			
SMA-15 on bitumen BND 60/90	2.53	3.17	3.4	0.81	0.95	0.19	29	0.17	0.88
SMA-15 on the polymeric-bitumen binders (BND 60/90 + 2% TPE)	2.53	2.81	4.0	1.2	0.93	0.41	3.6	0.14	0.92
SMA-15 on the polymeric-bitumen binders (BND 60/90 + 4% TPE)	2.54	2.20	4.6	1.7	0.94	0.54	44	0.09	0.95
SMA-15 on the polymeric-bitumen binders (BND 60/90 + 2% TPE + Azole)	2.52	2.75	3.6	1.1	0.95	0.43	38	0.15	0.95
SMA-15 on the polymeric-bitumen binders (BND 60/90 + 4% TPE+ Azole)	2.54	1.93	4.4	1.6	0.97	0.58	48	0.12	0.96
GOST 31015-2002	Not normal	1.0-4.0	At least 2.2	At least 0.65	At least 0.93	At least 0.18	At least 2.5 not more than 6.0	No more than 0.2	At least 0.85

with introduced Azole in an amount of 0.4% by weight of the polymeric-bitumen binders, as well as the difference spectrum (curve 3). As can be seen, the difference spectrum almost exactly repeats the thermoplastic elastomer structure including the presence of carbonyl C = O (1740 cm^{-1}) and vinyl C = C (1665 cm^{-1}) bonds. Hence, it can be highly likely argued that there is no chemical interaction between the thermoplastic elastomer and the adhesive.

With the introduction of the mixed thermoplastic elastomer into the bitumen a chemical interaction between thermoplastic elastomer and bitumen matrix occur by unsaturated C = C bonds with formation of a lightly crosslinked polymer within the polymeric-bitumen binders matrix. Thus, unstable double C = C bonds are transformed to weatherproof C-S-C bonds, whereby we obtain a polymeric-bitumen binder having enhanced weatherability and stability of basic performance properties.

Introduction of Azole in mixtured thermoplastic elastomer does not lead to a chemical reaction of the components, so Azole retains the properties of the adhesive additive in polymeric-bitumen binders. Upon that, this reduces the time of obtaining polymeric-bitumen binder, the resulting composition is less subject to thermal degradation what further extends the life of polymeric-bitumen binders.

Further studies were conducted by preparing Stone Mastic Asphalts (SMA-15) which were manufactured and tested according to standard methods provided for stone mastic asphalts according to GOST 31015-2002.

As seen from the results shown in Table 1, all SMA-15 samples met the standard requirements. It should be noted that introduction of the adhesion additive of mixed thermoplastic elastomer in binder leads to a slight increase in fracture toughness index upon rupture at 0°C. Increasing the fracture toughness index upon rupture of a rubble-mastic asphalt based on polymeric-bitumen binders is caused, apparently, by that the amount of binder in these cases is less than optimal because the greater the viscosity of the bitumen, the thicker is optimal film thickness. This fact also indicates that a greater amount of binder is in a structured state.

At the same time the strength of asphalt concrete at 20°C increases up to 35% depending on the composition of polymeric-bitumen binders and strength at 50°C increases from 40-100%. The greatest strength of the samples is reached by using polymeric-bitumen binders with addition of 4% thermoplastic elastomer and thermoplastic elastomer + Azole. This is, apparently, caused by a specific structuring effect of a polymer grid formed by molecules of the mixed thermoplastic elastomer at a positive temperature what determines the ability of polymeric-bitumen binders to highly elastic deformations.

Thus, the value of compressive strength for SMA-15 using polymeric-bitumen binders for positive temperatures higher than with conventional bitumen and at low temperatures (0°C) there was a slight increase in the rate of crack resistance at rupture.

Water resistance of stone mastic asphalts with introduction of the mixed thermoplastic elastomer additives remain high in the water saturation regime under vacuum. Table 1 shows that addition of the mixed thermoplastic elastomer a volumetric water saturation of samples is reduced from 3.17% to minimum 1.93% for the composition with BND 60/90 + 4% of thermoplastic elastomer and water resistance coefficient increases upon prolonged water saturation.

Shear resistance by the internal friction coefficient at 2% mixed thermoplastic elastomer content in bitumen is almost unchanged, but there is a sharp increase in adhesion index upon shear at 50°C.

To improve the physical and mechanical properties of cement concrete we have used sand with optimum grain

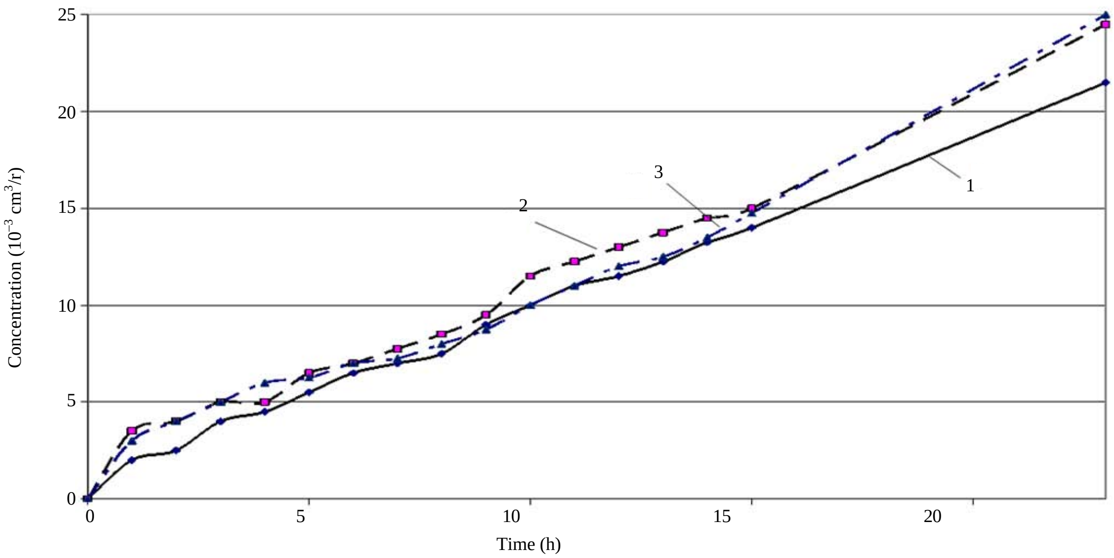

Fig. 3: Effect of superplasticizer S-3 on contraction of the cement paste: 1: without S-3; 2: 0.5% S-3; 3: 1% S-3; contraction: 10^{-3} cm^3/g

size and also chemical and mineral additives. In order to optimize the composition of a sand grain composition, a combination of three fractions were used: 5-1.25 mm, 1.235-0.315 mm and 0.315-0.14 mm. The ratio of fractions was chosen experimentally in terms of bulk density and specific surface area. By the results of researches it was found that the optimum content of 5-1.25 mm fraction is 60%, fraction 1.25-0.315 mm 20% and fraction 0.315-0.14 mm 20%. This fractions ratio provides a minimum sand void content with not a high specific surface area.

In a number of studies (Taylor *et al*., 2012) it was noted that addition of a filler in a binder composition allows relaxing strains in the course of cement structure formation increasing strength and deformability uniformity as well as to absorb the energy of cracks growth and stop it due to branching and as a consequence, improve physical and mechanical properties of cement. However, the major problems upon the use of mineral additives to the concrete binders are dispersibility and their amount that is allowed to introduce into cement without reducing its strength and the method of introduction of mineral additives in concrete (composed of blended cements or separately with cement). When using mineral additives more dense packing of the blended cement original matrix is reached due to distribution of the fine particles in the intergranular voids between more coarse cement grains and upon its hardening there occurs a more active interaction between the additive particles with calcium hydroxide generated by hydration of clinker minerals with formation of a high-strength low-basic and fine-grained calcium silicates. From this perspective, an efficient filler in cement concrete is microsilica suspension characterized because it features by small grain size and high activity with respect to calcium oxide. The microsilica suspension MK-85 was selected as a filler because it is the most active pozzolanic additive required for obtaining high-strength concrete.

To reduce the increased porosity of sand concrete, two superplasticizers different by their chemical structure have been selected to assess their effect on the cement hydration process. In the capacity of additives, we have selected a superplasticizer S-3 based on naphthalene and formaldehyde and Melflux 2651F on the basis of a polycarboxylate. Introduction of additives in cement paste makes it possible to slow the setting time. Slowing the hydration process can be traced by change the contraction of the cement paste.

As seen in Fig. 3, introduction of the superplasticizer S-3 slightly increases contraction in the first hour of cement hydration and then a contraction rate is reduced with an increase in dosage indicating the inhibiting role of the superplasticizer. Introduction of S-3 has little effect on the early setting and significantly affects the end of the cement setting, i.e., the additive S-3 inhibits hydration of cement in the induction period. Otherwise, cement contraction is affected by Melflux 2651 additive.

As seen in Fig. 4, introduction of the additive Melflux 2651F significantly affects the cement contraction. With increasing the additive dosage the cement contraction

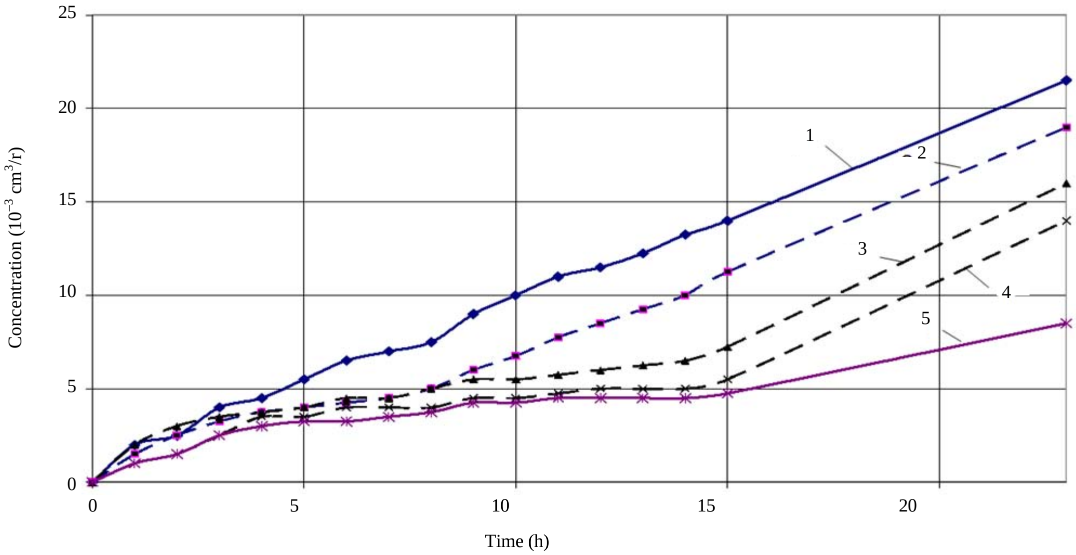

Fig. 4: Effect of Melflux superplasticizer on cement paste contraction: 1: without Melflux; 2: 0.25% Melflux; 3: 0.5% Melflux; 4: 0.75% Melflux; 5: 1% Melflux; contraction: 10^{-3} cm^3/g

Table 2: Composition and properties of the concrete mix and B80 class concrete

Composition No.	Material consumption (kg/m^3) Cement	Sand	Melflux 2651	MK-85	Water	Concrete mix consistency (OK) (cm)	Concrete mix density (kg/m^3)	Average compressive strength of concrete at the age (MPa) After thermal vacuum treatment	28 days
1	520	1700	2.08	26.0	140	16	2370	70.3	94.1
2	550	1680	2.20	27.5	140	16	2370	70.8	105.3
3	580	1660	2.32	29.0	141	17	2375	72.5	106.2

process slows down, too. When introducing the additive in an amount of 1% by cement weight induction period of hydration is extended to 15 h.

The research allowed founding that obtaining a high strength cement paste is possible through the mixed use of additives based on polycarboxylates filled with silica fume. Composition of B80 class fine concrete was selected on the basis of this research. Selection of the composition was carried out based on a sand with the optimum grain composition. In the concrete composition there was changed a cement content to achieve the required strength. The superplasticizer Melflux 2651F and microsilica MC-85 were used in the capacity of additives. The compositions of concretes are presented in Table 2. As can be seen from Table 2, obtaining a B80 grade concrete needs in 550 kg of cement per $1m^3$ concrete as further increase in flow rate does not lead to an increase in strength. The effective application of the developed high-strength fine-grained concrete composition its performance characteristics were studied. Since, high-strength concretes are characterized by increased cement content, the role of the elastic modulus and cement paste shrinkage on deformation characteristics of concrete becomes more significant. With a decrease in the size of the aggregates, shrinkage deformation increases and microcracks are distributed more discrete in its entirety. Therefore, shrinkage deformations in the fine-grained concrete can be 1.5-2 times higher than that of equally strength heavy concrete with large aggregates.

The researchers found that reduction in shrinkage is possible by optimizing the sand grading due to reduction of its void content and joint action of plasticizing additives and a filler. So, shrinkage of the developed sand concrete with B80 class compressive strength has decreased by 61% what is almost close to that of coarse heavy concrete. Comparable performance properties of high-strength fine-grained and coarse concretes are shown in Table 3.

As can be seen from Table 3, sand concrete has a higher tensile strength in bending in comparison with the coarse concrete and modulus of elasticity is slightly inferior to the values of coarse concrete. The increase in bending strength of fine-grained concrete is related with increase in the number of contacts between cement paste

Table 3: Properties of high-strength fine-grained and coarse concretes

	Concrete composition (kg/m^3)					Compressive strength, MPa	Concrete bending strength,	Elastic modulus	Frost
No.	Cement	Crushed stone	Sand	Additive	Filler	(after 28 days)	MPa (after 28 days)	(MPa)	resistance
1*	480	990	750	100 MB10-30S	-	98.1	7.12	44200	-
2	550	-	1680	2.2 Melflux	27.5 MK	106.2	9.82	43200	F_2 400

*Data by Kaprielov *et al.* (010)

and a filler. Furthermore, the combined use of microsilica and superplasticizer reduces a porosity in the contact zone of the filler with cement paste (as shown previously) what also increases the tensile strength in bending. Reduced modulus of elasticity is associated with an increased volume of cement paste in concrete. Frost resistance of the obtained concrete is twice the statutory value.

Analysis of the data suggests that a stone mastic asphalt based on polymeric-bitumen binders is more resistant to formation of corrugations and waviness under conditions promoting to their formation and is more shear resistant. The modified fine concrete obtained as a result of work has great strength and wear resistance, respectively as well as high resistance to frost, thus increasing pavement service life.

CONCLUSION

As a result of the research we have shown the feasibility of using a mixed thermoplastic elastomer as an additive in bitumen, because its use allows obtaining the materials characterized by high strength and shear resistance at a positive temperature and good deformability at temperatures below freezing.

It was found that the fine-grained concrete cement has a higher tensile strength in bending than the coarse one what positively affects the performance and durability of road pavements.

Thus, the research allows achievement goals to increase the strength characteristics and durability of materials for road construction.

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