Effects of structural formation in the implementation of the technology for obtaining asphalt concrete mixtures with phosphogypsum and other additives

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Abstract. The paper considers the effects of structural formation in dispersed systems and composite materials obtained using the technology of asphalt concrete with up to 30% phosphogypsum included in the mixture. The study of physicochemical and consumer properties of such systems and materials involved using the method of study of surface effects (measurement of a contact angle). One of such materials is bitumen with a non-traditional additive polyethylene terephthalate. The presented microphotographs of modified asphalt concrete mixtures allow to study the changes in the state of bitumen surface. Differential-scanning calorimetry is used to register thermal effects arising from the implementation of technology to modify the properties of materials. It is revealed that obtaining asphalt concrete mixture by pelletizing provides the necessary indicators of the hardened material’s compressive strength. It is determined that the water resistance of asphalt concrete increases at simultaneous introduction of polyethylene terephthalate and industrial waste powder — phosphogypsum — into dispersed system. It is also determined that the specified additives synergistically affect the consumer properties of bitumen and achieve the positive effect of structural formation in asphalt-binding materials, which reveals new prospects of their use in road building.

Keywords: composite materials, disperse systems, asphalt concrete mixtures, modification, phosphogypsum, polyethylene terephthalate additive, pelletizing, structural formation, consumer properties

1. Introduction

The term "structure" in composite (dispersed) materials means a spatial framework formed by the bonds of atoms, ions, molecules, micelles, crystalline terminations, and particles of colloidal sizes [1].

Coagulation (coagulation-tixotropic) and condensation (condensation-crystallization) dispersed systems (DS) are distinguished by the type of contacts. In coagulation DS, the particles interact through a layer of liquid dispersed medium and are bound by the van der Waals attractive force. Condensation DSs are formed in the extraction of a new phase from oversaturated vapors, melts, and solutions [2].

The structure formation effect and detailed study of colloidal-chemical properties [3] are the basis for the creation of most modern composite materials. P.A. Rebinder formalized the main provisions for obtaining ideal composites. He argued: "The easiest way to increase the strength of any solid to almost the ideal ceiling is to grind it to particles that are in order of magnitude corresponding to the distances between the dangerous weak points. If such particles are densely packed or glued with the finest interlayers, the resulting material will be dense, impermeable to liquids and gases, high-strength and durable" [4].

Asphalt concrete is a composite material in which crushed stone, river sand and mineral powder are used as fillers, and bitumen acts as a binding agent. The main structure-forming component of the mixture is a mineral powder, a finely dispersed fraction with a highly developed specific surface. According to [5], up to 95% of the bitumen introduced into the asphalt concrete mixture - the most expensive component of the mixture - is used for wetting the surface of the mineral powder.

Compliance with P.A. Rebinder's requirements is possible due to pelletizing mineral powder (with bitumen as a binder) [6]. Previously [6] we obtained granulated asphalt binder, which has high strength,
minimum water saturation, lack of tendency to clumping. Further research has allowed us to develop the technology framework aimed at solving a global environmental problem — phosphogypsum utilization (waste phosphoric acid and fertilizer production). The accumulated volumes of this product in Russia are estimated at hundreds of millions of tons and are increasing annually. Large useful areas are wasted on them, and they impose a real threat to the environment.

The first attempts to use phosphogypsum as a mineral powder for asphalt concrete mixture, which is obtained by pelleting technology, allowed the researchers to obtain a material that meets the GOST requirements for most physicochemical and consumer properties, except for water resistance. As a result of long searches, it was possible to find a modifier for bitumen that provides the necessary level of water resistance of asphalt concrete. As such, it is now possible to use household waste polyethylene terephthalate (PET), from which a large share of plastic containers (plastic bottles in particular) is made. The found technical solution is protected by the RF patent [7]. Taking into account the results above, the industrial implementation of the developed technology will allow to lay not only quality road pavements, but also contribute to the solution of the environmental problem — PET waste utilization (estimated in millions of tons annually).

It should be noted that the developed technology is based on the effects of structural formation, the implementation mechanisms of which have not yet been sufficiently studied. In this regard, the new information resulting from our studies appears very relevant.

2. Work objective

The aim of the work is to scientifically justify the effect of the increase of water resistance of asphalt concrete described earlier [6, 7] using phosphogypsum as a mineral powder when modifying bitumen with polyethylene terephthalate. The use of polymer-bitumen binders is among the actively implemented world technologies for construction and repair of road surfaces. In Russia, copolymers of butadiene and styrene as well as solutions of synthetic rubbers are used to modify bitumen [8]. The purpose of introducing polymers into bitumen is to increase their deformability at low ambient temperatures (about 0°C), heat resistance, and elasticity.

Improved performance properties of bitumen can be achieved when the polymer dissolves or swells in the dispersion medium of bitumen, forming a structural mesh. In contrast to thermoelastic polymers, the molecular structure of polyethylene terephthalate appears to be linear, and therefore the mechanism of polymer exposure to bitumen should be different from the one described previously. In addition, in the process of pelleting mineral powder particles form an ordered structure with interlayers of a binder of minimum thickness between them (meets the requirements of P.A. Rebinder).

The nature of the interaction between bitumen and polymer in this case is unknown. This calls for the study of a mechanism to increase the water resistance of asphalt concrete with added phosphogypsum. The importance of such works is related to the introduction of technology of manufacture of new asphalt concrete mixtures and achieving high ecological and economic effect. Specificity of the developed technology is presented in [9].

3. Experiment

To achieve this goal, modern methods are used to study the structure of obtained materials, including electronic microscopy and differential scanning calorimetry to determine phase transitions in the source systems and their modified states. At the final stage, we evaluate the stability at storage of operational (consumer) properties of the received composite materials according to GOST 12801-98. Conducting theoretical research in this case is problematic. The process of asphalt concrete mixture formation involves taking into account the mutual influence of many factors on each other, the degree of influence of which on the final result is not quite obvious.

4. Results discussion

The water resistance of asphalt concrete is the most important factor determining the durability of the road surface. This factor has the greatest impact during the off-season, when freezing alternates with thaws, and moisture penetrates the coating and expands when there is the next freezing, thus tearing it. However, studies of water resistance of asphalt concrete based on phosphogypsum were conducted at room temperature, which excludes such an effect. The strength of samples based on traditionally used mineral powder and similar with the added phosphogypsum are comparable, but the water resistance of the latter is significantly lower. Ensuring the required strength of the material when using phosphogypsum is evidence of its sufficient adhesion to bitumen. The decrease in water resistance is probably due to specific chemical problems.
The increase in water resistance of the material when introducing PET into bitumen can be explained in two ways. The first explanation assumes the formation of a true solution of bitumen with polyethylene terephthalate, which is thermodynamically stable at all temperatures and has high water resistance. The second theory assumes that the mixture of bitumen and plastic during cooling is divided into initial phases. It is possible that a new material structure is formed which corresponds to an increase in internal pressure in the system which prevents water from diffusing into the composite structure.

A simple method to study surface effects is to measure the contact angle $\theta_0$ [3]. Its value allows to determine the ratio of cohesion forces in the liquid phase and adhesion forces in the contact area of liquid and solid phases. Drops of bitumen were applied on the glass slides with PET additives (5, 10, 15, 20 wt. %), kept at 100 °C for 20 minutes, then we surveyed the surface and measured the contact angle (Fig. 1).

![Figure 1. Photographs of bitumen drops with 5 (a) and 20 (b) wt. % of PET content.](image)

As seen in Table 1, increasing PET content in bitumen leads to a sharp increase in the equilibrium contact angle of the surface.

| Polymer concentration, % | 0  | 5  | 10 | 15 | 20 |
|--------------------------|----|----|----|----|----|
| Equilibrium contact angle, deg. | 6  | 28 | 30 | 30 | 120 |

There are several possible explanations to that:
- a) increased plastics content reduces the adhesion of bitumen to the hard surface;
- b) increase in plastic content enhances cohesion of liquid;
- c) both of the above factors apply simultaneously.

The single study we conducted is not enough to give an unambiguous answer to the nature of the change in water resistance of the material when introducing PET in bitumen. Note that the melting point of PET is 260 °C, and softening of bitumen happens earlier. When PET is introduced into bitumen heated to its melting point, a visually homogeneous mass is formed during mixing. This leads to the initial theory of a true solution of plastic in bitumen. The question is: what state will PET be in when the mixture is cooled to a temperature below its melting point?

It is reasonable to assume that when cooled, PET can remain in bitumen, forming a homogeneous mixture, as well as to form dispersion in the bituminous matrix. Since it is impossible to identify plastic particles in the bitumen mass, we conducted an additional experiment in the cyclohexanone medium. It is a good solvent for this polymer. When heated, we obtained a homogeneous solution, and when cooled, we observed its dispersion. A picture of dispersion of PET in cyclohexanone is shown in Fig. 2. The maximum particle size of the dispersed PET is 5-8 microns.

Coagulation of small particles with the formation of enlarged aggregates is a factor that negatively affects the homogeneity of the product.
At first glance, using bitumen as a solvent makes coagulation more difficult, i.e. conditions are created to distribute small particles of PET uniformly in the binder volume. However, the theory was not confirmed after observing the behavior of the modified bitumen during its cooling. This indicates that intermolecular interaction between PET particles is more intensive than their interaction with bitumen, despite the direct phase contact in the latter case. It becomes clear why the equilibrium contact angle increases when the content of PET in bitumen increases as well.

Consequently, the provision about the cohesive force strengthening in the binder is confirmed when PET is added. However, the problem of specifying the form of plastic presence in the binder (dispersion or solution) remains open. To solve it, we studied samples of bitumen, PET, and modified bitumen (PET 10% added) using DSC 200 Phox by NETZSCH for differential scanning calorimetry. The method consisted in recording thermal effects in the studied sample of PET when heated at a constant rate compared to a standard sample (in this case — an empty crucible).

As seen in the thermograms (Fig. 3), the sample of PET (curve 2) has three transitions. The first transition is observed in the temperature range corresponding to the beginning of glass transition (76.5 °C). This process consumes energy due to the increase in mobility of polymer molecules during its transition from amorphous to glassy state. The second transition (155 °C) corresponds to the beginning of polymer crystallization. In this case, energy is released due to the arrangement of molecules in the lattice, limiting their mobility. The third transition (with absorption of thermal energy) starts at 200 °C and ends at about 260 °C. It corresponds to the melting interval of this polymer, accompanied by the removal of restrictions on the mobility of molecules. An important thing to note is that peak areas during crystallization of the material are almost completely indistinguishable from the peak areas during its melting, which indicates the amorphous state of the modifier (PET) and disorder of macromolecules.

Figure 2. General view of the dispersion of PET in cyclohexanone (30 microns).
Figure 3. Thermograms taken for samples of bitumen (1), PET modifier (2), and bitumen-PET modifier system (3).

The curve 1 shows the transition that determines the temperature of glassing of bitumen in the range of temperatures (from -10.9 to 4.6 °C). The thermogram of the bitumen sample with the PET additive (curve 3) is quite diverse. It has transitions corresponding to the temperatures of bitumen glass transition and PET, as well as the crystallization and melting temperatures of the modifier. The latter are not expressed explicitly, which is explained by the low content of the additive in the composite material (1 wt. %). One specific aspect of this thermogram is a new transition in the temperature range (20.4 - 33.4 °C) corresponding to the glass transition.

Analysis of Fig. 3 allows us to draw some important conclusions. First, the presence of characteristic transitions, which are inherent in the original components, on the curve 3 indicates the absence of their qualitative mixing. There is no true solution formation; the modifier is distributed in bitumen in the dispersion form [10]. Secondly, the decrease of energy to support a given mode of temperature change indicates the emergence of additional bonds that limit the internal mobility of the system. Third, the glass transition temperature of the mixture (20.4 - 33.4 °C) determines the moment of coagulation of dispersed particles of PET with the formation of sediment in bitumen [11].

This process can be presented as follows. When PET is dispersed, the work is done in bitumen to create new interfacial areas and increase the internal energy of the system. When the mixture cools down, coagulation of PET particles generates energy, determining the transition to glass transition [12]. The disperse phase of the modifier, which is distributed in the bitumen volume, acts as power centers, in a way. These centers create additional internal pressure in the system to prevent fluid from entering the binder. In the theory of surface phenomena, this is called the structuring effect, which most nanoeffects are based on [13].

The research made it possible to clarify the mechanism of PET influence on bitumen, which provides an increase of water resistance of asphalt concrete. Microphotographs of asphalt binder samples with the phosphogypsum powder additive obtained from PET-free bitumen (Fig. 4, a) and the modifier additive (Fig. 4, b) complete the picture and serve in favor of the theory of dispersion of the modifying additive of polyethylene terephthalate.
Figure 4. Microphotographs of a bitumen-phosphogypsum system (a) and bitumen with a PET-phosphogypsum additive (b).

Phosphogypsum crystals shown in Fig. 4, a are evenly wetted with bitumen, and their surface is smooth. The introduction of PET into the binder leads to a large number of small inclusions of the modifying additive on the crystallized surface (Fig. 4, b). Thus, the specified modifier is distributed in the asphalt binder as dispersed formations, which interact with each other at a distance of an additionally formed field of intermolecular forces. The presence of such a field prevents diffusion of moisture into the depth of the created composite material and provides an answer to a number of questions raised earlier in [14].

5. Conclusion
Recycling of industrial and domestic waste in modern conditions is an urgent problem. The results of numerous studies in this area tend to allow recycling in small quantities, which is not a global solution. The data we have obtained is of great interest in terms of updating and developing road construction technologies. In particular, it is the first time polyethylene terephthalate is offered to be used as a modifier of road bitumen, and we studied the problems of physicochemical mechanics of the pelletized systems with the specified additive with phosphogypsum being in system at the same time. It was found out that the obtained composite materials (asphalt concrete mixtures) can be stored in a cooled state for a long time without losing their operational (consumer) properties. This makes it possible to manufacture them for future use without limiting the production volume.

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