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Porosity Of The Filler For Asphalt Concrete As Controlling Factor Of Structure Formation

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High-performance paving materials are currently in strong demand. Because of this, research works concerting relations between structure and operational properties of asphalt concretes are of high importance. The present work is devoted to investigation of structure formation process of bitumen-mineral mixes. Dependencies between structure of the pore space of siliceous mineral fillers and characteristics of structure formation process are examined. Pores in fillers are broken up into two categories. In the first category there are pores large enough to guarantee the validity of Poiseuille law; such pores (active pores) are involved in the process of physical adsorption of bituminous components. The second category composed of small pores (passive pores) which are not involved in the adsorption process. The parameters of the pore space of mineral materials (surface area, porosity and micro-porosity) and activity of the interaction between filler and bitumen (bitumen adsorption index, quantity of adsorption sites) are investigated. To effectively control the values of macroscopic properties it is necessary to determine primary structural factors; it is shown that volumetric proportion of the active and passive pores is one of such factors. In particular, reduce of the bitumen adsorption index can be achieved by lowering such ratio. It is also revealed that splitting of diatomite grains during grinding takes place for weak spots – macropores (active pores) the ratio of volume of active pores to volume of passive ones changes during grinding.

Keywords: porosity, active pores, passive pores, adsorption, diatomite, mineral filler, silica

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Introduction

Carbonate mineral powders which are used during production of asphalt concretes are rare in some regions. There were several attempts to use different technogenic wastes in order to expand the mineral resource base and to find alternatives for conventional fillers. While such attempts were conducted in several regions, using the non-traditional fillers in asphalt concretes requires solid justification of possibility of their use. The latter including evaluation of possibility to obtain durable road composite based on mentioned fillers.

The mineral filler is an important structural component. Its main purpose is to transfer the “bulk phase” of bitumen into the “film state”. When mixed with hot bitumen, mineral powder is subject to complex physical and chemical processes. The former are diffusion of light fractions of bitumen into the grains of mineral powder and physical adsorption of light fractions on the surface of grains. The latter are chemisorption on the interface “bitumen - mineral filler” and alteration of the mineral material during interaction with the bitumen [1, 2]. Analysis of different information sources reveals that to obtain asphalt concrete with high physical, mechanical and performance properties it is possible to use mineral powders made of basic and acidic rocks [3…6]. Also, the structure of surface and pore space of mineral powder grains affects the intensity of the interaction of the filler and bitumen.

During manufacture, when bitumen and porous mineral powder are mixed together, selective filtration of bitumen components into the pores takes place. The tar and oils of bitumen concentrate in the surface micropores, whilst other part of bitumen penetrates into the material. Because of such process, the components of bitumen with high activity (asphaltenes and stable radicals) are exposed to mineral materials and start to react with them. The reaction leads to formation of strong bonds which, in turn, increase the strength of the structure of asphalt concrete [7, 8].

At the same time, excessive diffusion of light fractions of bitumen into the grain material may cause the depletion of binder. Due to this, the aging process accelerates and service life of asphalt concrete pavement reduces. Thus, the porosity of the mineral material which is used as filler in asphalt composition should be sufficient to form a strong structure of asphalt concrete, but should not exceed the threshold value at which the bitumen will age.

Methods

To discover the possibilities of controlling the early structure formation process for organic-mineral mixtures, during research we have examined parameter of the pore space of mineral materials (including surface area, porosity and micro-porosity), bitumen adsorption index and quantity of adsorption centers. The latter parameters characterize variation in the activity of the interaction of filler with bitumen. The surface area and volume of the mesopores and micropores (with diameter less than 200 nm) were determined by nitrogen adsorption porosimetry using the Brunauer-Emmett-Teller (BET) theory and Barrett-Joyner-Halenda (BJH) analysis. The essence of the measurement method for bitumen adsorption index is in determination of quantity of oil which, when mixed with 100 cm^3 of powder, will have a predetermined consistency. The amount of active acid sites was determined by the volumetric capacity of siliceous mineral materials in relation to calcium ions by procedures which are described in [14]. Porosity of mineral material is the ratio of the average density (ρ_m, g/cm^3) and the true density (ρ, g/cm^3) and was calculated as

$$V_{por} = \left(1 - \frac{\rho_m}{\rho}\right) \cdot 100\% .$$

Analysis of the pore space

Not every pore participates in the processes of filtration of light fractions of the bitumen. Adsorption of components of the bitumen takes place only in case of open pores with geometry which guarantees the validity of Poiseuille law for a cylindrical capillary:

$$\frac{dv}{dt} = \frac{(P_1 - P_0)\pi \cdot R^4}{8 \cdot \eta \cdot L} > 0,$$

where $P_1 - P_0$ – pressure difference at the ends of the capillary; $P_1 = \frac{2\sigma}{R}\cos(\theta)$ – capillary pressure, Pa, calculated in accordance with the Laplace's law; $\frac{dv}{dt}$ – volumetric flow of liquid, m^3/s; R – radius of the capillary, m; η – dynamic viscosity, Pa·s; L – length of capillary, m.

The pore space of mineral material can be divided into active pores which absorb light fraction and passive pores with such geometric sizes that the Poiseuille law is no longer valid. Thus, the obvious choice for controlling factor is the volumetric ratio of active and passive pores. Alteration of the mentioned ratio allows management of the structure formation process during interaction of bitumen with mineral materials.

The boundary between active and passive pores, which can be considered as “activity limit” and corresponds to pores which are no longer absorb light fraction of bitumen ($\frac{dv}{dt}$ = 0), can be determined from the relation

$$\frac{\left(\frac{2\sigma}{R}\cos(\theta) - P_0\right) \cdot \pi \cdot R^4}{8 \cdot \eta \cdot L} = 0 .$$

Taking into account that for activity limit we have $\theta = 0^o$, where θ – contact angle (pore no longer absorb the light fraction of bitumen; typical values of other parameters: σ = 0,0375 N/m, P_0 = 101325 Pa [9]), the radius of the capillary corresponding to activity limit can be determined from the latter relation:

$$R = \frac{2\sigma\cos(\theta)}{P_0}$$

If we suppose that the light fraction of bitumen completely wet the surface of mineral material, than passive pores are pores with less than 740 nm radius.

Changing the ratio of the volume of passive pores and the volume of active pores allow to regulate bitumen adsorption index of porous mineral materials and provide the possibility of their use as fillers in bituminous concrete.

Experimental results and discussion

The structure of the pore space of mineral powder is controlled by means of physical-mechanical and physical-chemical methods. The former method consists in grinding of mineral powder; during such process small grains with passive pores are produced from large grains with active pores. The latter one consists in modification of grain by means active surface modifier [10…12]. These methods are mostly suitable for porous mineral powders which are chemically inert to bitumen. Among others, such chemically inert (to active functional groups of bitumen) materials are powders based on silica-containing minerals (tripolite, gaize, perlite, diatomite, etc.).

The volume of active pores is the primary factor of influence for the intensity of interaction between bitumen and silica-containing materials. The intensity of interaction depends to the less extent on the number of adsorption sites on the grains' surface.

This is due to interaction of bitumen and porous silica-containing mineral material is mostly determined by physical adsorption without formation of strong chemical bonds [13]. By means of nitrogen porosimetry we can directly study the structure formation process of bituminous mixtures and examine the influence of pore space of mineral filler.

Two-factor composite experimental design was implemented. Parameters of grinding (X_1 – Rotating speed, rpm; X_2 – time of grinding, min) are selected as predictors. It was also proved during the research that polynomial regression model

$$Y = B_0+B_1\cdot X_1+B_2\cdot X_2+B_{12}\cdot X_1\cdot X_2+B_{11}\cdot X_1^2+B_{22}\cdot X_2^2$$

is suitable (hypothesis test for adequacy by means of F-criterion) as a description.

Materials with a similar chemical composition but with different pore structure were selected as fillers: quartz sand and diatomite. Amount of active adsorption sites were determined by with help of method described in [14]. Zero levels and half-variations for experimental designs are summarized in Table 1.

Table 1. Zero levels and half-variations of experimental designs.

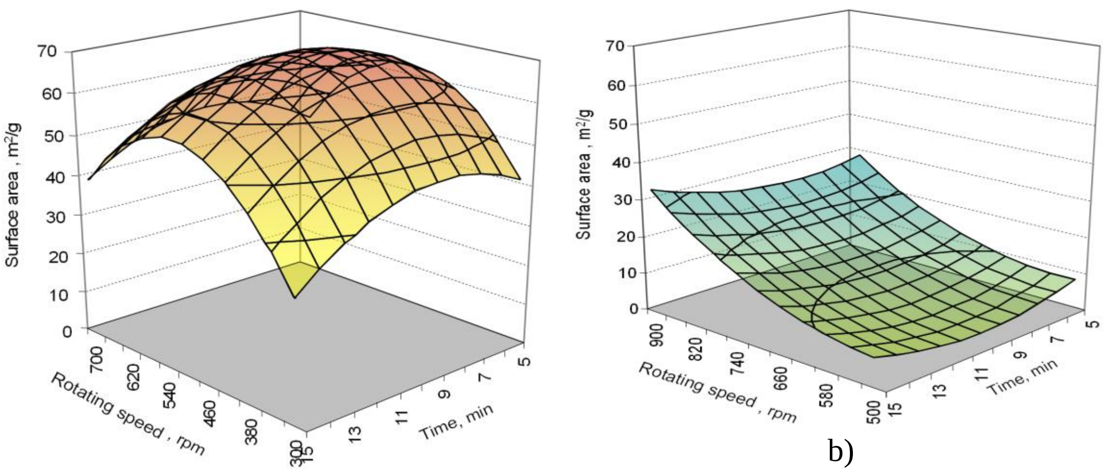
Mineral filler	Zero level		Half-variation	
	X_1, rpm	X_2, min	X_1, rpm	X_2, min
Diatomite	500	10	200	5
Quartz sand	700	10	200	5

Parameters of obtained statistical models are shown in Table 2.

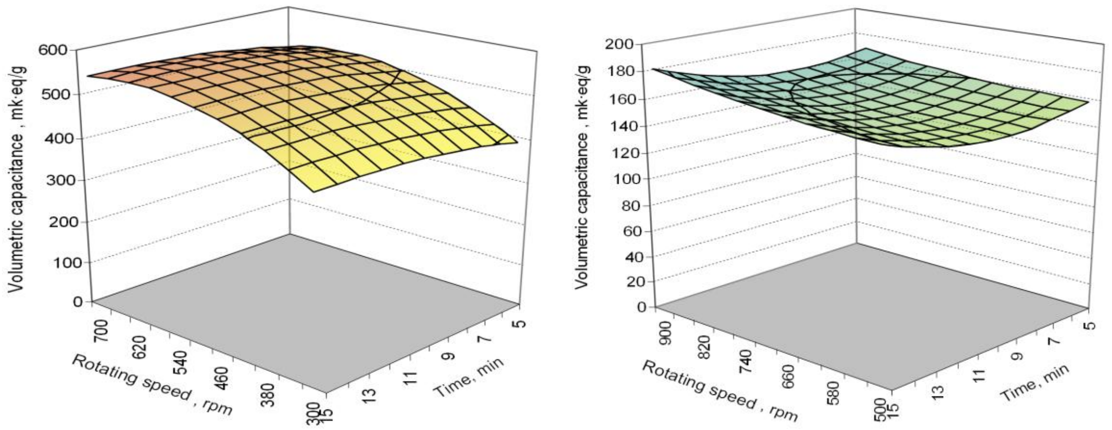
Table 2. Parameters of statistical models.

Response variable	Type of filler	Parameters of regression model					
		B_0	B_1	B_2	B_{12}	B_{11}	B_{22}
Surface area (BET), {m^2/g}	Diatomite	69.477	2.7403	–3.3152	2.199	–21.060	–10.352
	Quartz sand	9.153	11.592	1.2462	1.3175	5.6005	4.6205
Amount of active adsorption sites, {mk·eq/g}	Diatomite	532.30	59.654	19.801	0.300	–50.994	–14.169
	Quartz sand	152.87	7.639	5.440	1.853	3.098	12.898
Porosity, {%}	Diatomite	40.4	–2.3266	–0.8114	1.2	2.3688	0.94375
	Quartz sand	49.7	3.4508	1.1547	4.9	–5.75	–8.95
Volume of micropores (d < 200 nm), {10^{-3} cm^3/g}	Diatomite	124.41	15.185	–1.1607	–4.6025	–33.67	–16.162
	Quartz sand	15.670	15.738	1.6418	0.230	6.0869	4.7544
Bitumen adsorption index	Diatomite	129.40	–21.865	–12.194	5.2825	11.582	4.7219
	Quartz sand	63.880	20.373	7.5868	–1.2575	–9.5337	–7.7812

Response surfaces are presented on Figure 1 and Figure 2.

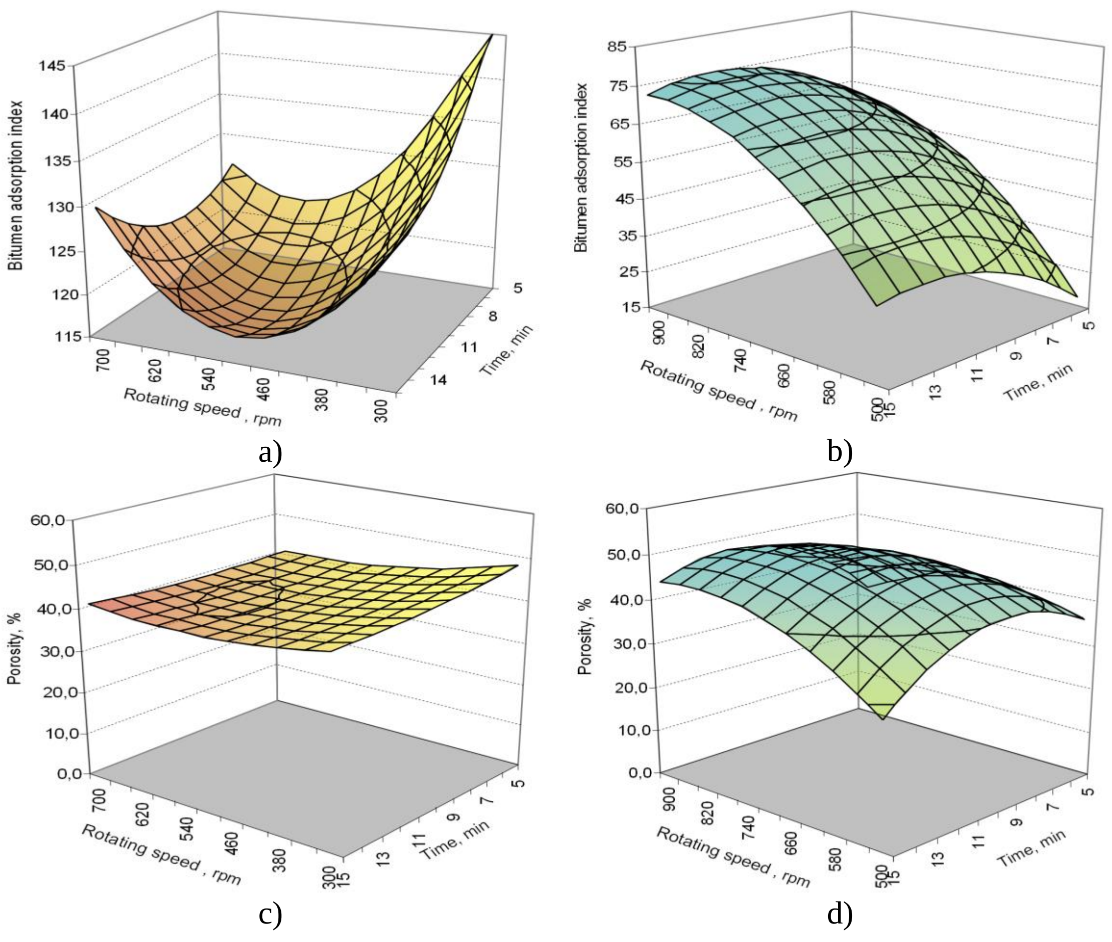


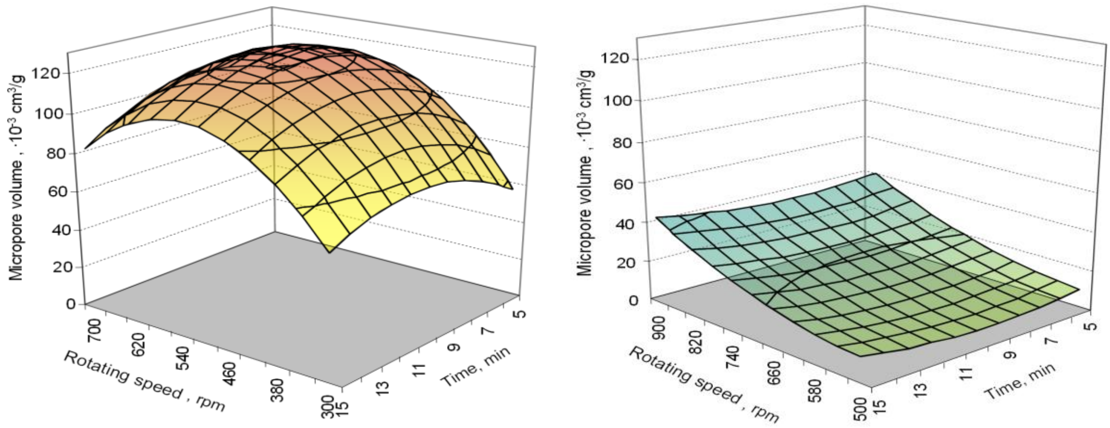
a) b)



c) d)

Figure 1. Response surfaces for regression models of surface area (BET) and volumetric capacitance for diatomite (a, c) and quartz sand (b, d)





e) f)

Figure 2. Response surfaces for regression models of bitumen adsorption index, porosity and volume of micropores (with diameter less 200 nm) for diatomite (a, c, e) and quartz sand (b, d, f)

It is clear from the obtained results that both surface area and amount of active adsorption sites on the surface of particles grow together with the increase of rotation speed and time of grinding (Fig. 1); at the same time, total porosity of the mineral fillers does not vary to the large extent. There are also combinations of predictors corresponding to local maxima of response variables. In turn, growth of the surface area and number of active adsorption sites leads to increase of bitumen adsorption index. Diatomite-based filler is characterized by relatively low values of the latter parameter (Fig. 2). It is obvious that for siliceous mineral materials bitumen adsorption index is affected mostly by volume of pores which adsorb the components of bitumen, and not by number of chemical bonds.

To find out the primary factors influencing the activity of silica mineral powder it is necessary to examine alteration process of the structure of internal pore space. For the quartz sand, volumes of active and passive pores increase when the mineral is grinded. Growth of mentioned volumes leads to increase of bitumen adsorption index for milled mineral. On the contrary, alteration of grinding parameters for diatomite does not significantly alter total porosity. It we take into account fraction of pores with diameters of 500 nm and lower, than there is a maximum of such fraction for certain combination of predictors. This maximum corresponds to the minimum of bitumen adsorption index. Reduction of bitumen adsorption index is the consequence of two simultaneous processes: for active pores, the volume decreases, while for passive ones it increases. This is due to the fact that splitting of diatomite grains during grinding takes place for weak spots – macropores (active pores). Thus, the ratio of volume of active pores to volume of passive ones changes (Figure 3).

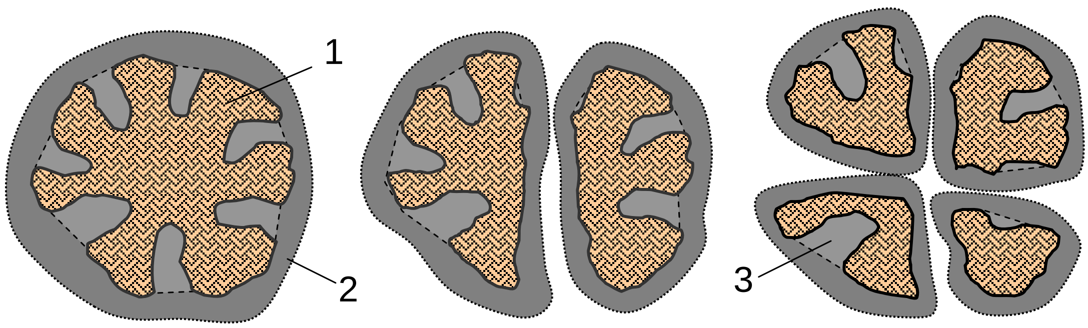


Figure 3. Schematic representation of structural alteration of the pore space: 1 – grain of the filler; 2 – adsorption-solvation film of bitumen (mostly formed by asphaltenes); 3 – light fractions of bitumen adsorbed by active pores

Conclusion

To effectively control the values of macroscopic properties it is necessary to determine primary structural factors; there were attempts to do so by means of experimental [11] and numerical [15] investigations.

It was shown during the research that pore space of mineral material can be divided into active and passive pores; former absorb light fraction of bitumen, while for the latter this does not takes place. Volumetric ratio of active pores to passive ones is the primary factor which affects both adsorption process and macroscopic properties of the asphalt concrete.

To control the structure formation of bitumen-mineral mixtures it is necessary to adjust the mentioned ratio; such adjustment leads to alteration in ratio of free and structured bitumen.

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