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Wettability and Surface Free Energy of Mineral-Asphalt Mixtures with Dolomite and Recycled Aggregate

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Abstract. The study on the wetting properties and surface free energy (SFE) of mineral-asphalt mixtures was presented in the paper. The composition of the two mineral-asphalt mixtures was prepared: the mixtures with dolomite and the mixtures with dolomite and recycled ceramic aggregate. The use of different aggregates results in diversification of the wetting properties in porous bituminous mixtures. The microstructure was shown based on the SEM study. The wetting properties of mineral-asphalt mixtures were determined by measuring the contact angle of their surface using water as measuring liquid. Measurements were carried out immediately after the time of application of the drops. The total surface free energy (SFE) was determined using the Neumann method. While analysing the examination results it can be noticed that the values of contact angles depends on the type of aggregate used in mixtures and the smoothness of mineral-asphalt mixtures surface. The highest contact angle was noticed for the bituminous mixture with dolomite aggregate on flat surface. The smallest contact angle with water was obtained for the mineral-asphalt mixture with dolomite and recycled ceramic aggregate on rough surface. This is due to the physical characteristics of this aggregate. Ceramic aggregate is characterized by the high absorbability. This indicates an increased wettability and adhesion properties.

1. Introduction

Most products, after their exploitation, end up at a landfill site. On the one hand, the objective is to recycle the exploited products; on the other hand, the search for substitutes of natural substrates among organic waste matter is common in the manufacturing of products [1-3]. There is a specific group of products that cannot be used in primary production after they have been exploited, such as ceramic products. The complicated processes that occur during heat treatment of clay irretrievably transform them into substances with different physical parameters and it is no longer possible for them to recover their natural state. Thus, the ways to utilize ceramic materials are sought in other branches of the industry. The main solution that is proposed is the application of crushed ceramic as composites filler. Despite extensive research on ceramics in concrete and mortar [4-7], no studies that would consider the application of these aggregates in mixtures used in road engineering are available.

The mixtures of composites have been designed to be applied in road engineering. The content of recycled ceramic aggregate in the prepared mineral asphalt mixtures was about 30%. A mixture consisting entirely of a traditional, dolomite aggregate was used as a comparative mixture.



The use of different aggregate and different smoothness of the mineral-asphalt mixtures surface results in different wetting properties and roughness in porous bituminous mixtures. According to the literature, the contact angle of the materials is an indicator of the wetting ability [1]. The contact angle can be used for determining the surface free energy (SFE) and the adhesion work. Many factors influence the contact angle, including physical and chemical homogeneity, roughness and surface contamination, type of measuring liquid, humidity etc. In the physicochemical assessment of the composites, the key parameter is SFE. There are many methods for direct determination of the SFE of a liquid. Due to the lack of direct methods for determining SFE for solids, indirect methods are used, which include the methods of measuring the contact angle and calculating SFE on this basis [8]. In this article, the Neumann model, which constitutes one of the most common methods of calculating SFE, was used in order to determine this parameter.

2. Materials and method

The basic mixture component that was supposed to be a substitute for a traditional aggregate included ceramic sanitary waste products. The waste with the approximate size of 20 x 40 cm was transported to a laboratory and preliminarily crushed in a ball grinder to the size of 2-4cm. The material prepared this way underwent the process of crushing in a jaw crusher.

Dolomite grit was used as a comparative aggregate. The analysis of basic technical parameters of examined aggregates has been presented in Table 1 [9].

Table 1. Technical parameters of aggregates used in the analysis [9].

Parameters	Dolomite	Sanitary ceramics
Specific density (kg/dm³)	2.4-2.8	2.64
Bulk density (kg/dm³)	2.2-2.6	2.36
Compressive strength (MPa)	60-180	400-600
Elasticity modulus (GPa)	18-48	40-70
Thermal expansion coefficient (10⁻⁵ α_t)	0.3-1.2	0.6-0.7
Absorbability (%)	0.3-1.2	1.53

Road bitumen 50/70 was used as a binder in mineral asphalt mixture. The basic technical parameters of asphalt are as following: penetration in 25°C – 50 – 701/10mm, softening temperature 46-54°C, breaking point ≤ -8°C, and ignition temperature ≥ 230°C. Limestone filler was applied as a filling aggregate in the mixtures. It is widely used in bituminous mixtures and surface treatment for roads, airfields and other trafficked areas.

The development of mineral asphalt mixture has commenced with meeting the requirements for mixtures [9]. The research programme assumed the production of two batches of mixtures. The first batch was a mixture intended for a wearing course, made of dolomite aggregate and ceramics (WC-1) and the second one was a mixture intended for a wearing course, consisting solely of dolomite aggregate (WC-2). It was assumed that the laboratory formula was developed for asphalt concrete intended for a wearing course with 0-11.2mm grain size and for surfaces of KR1-2 category traffic load. The formulas were devised on the basis of regulations [10] and [9]. The final composition of the mixtures is presented in Table 2.

The density of mineral asphalt mixture was determined in accordance with the regulation [11]. It was assumed that the mass of analysed specimen expressed in grams should be at least 50 times greater than the thickest grains of the aggregate found in mineral asphalt mixture. The specimens were crushed into respective grains or clusters so that the diameter of clusters did not exceed 6mm. In the case of the compacted specimen, before crushing it was placed in the dryer with the operating temperature of 110°C and heated until it was possible to crush it. Next test involved the determination

of bulk density of mineral asphalt mixture. The test was conducted with the use of Marshall specimens. Each specimen was weighed and immersed in a water bath for 40 minutes.

Table 2. Composition of mineral mixture (MM) and mineral asphalt mixture (MMA).

Components	WC-1		WC-2	
	% content in			
	MM	MMA	MM	MMA
Limestone filler	9	8.3	6	5.6
0/2 quartz	16.0	15.0	22	20.7
0/4 ceramics	15.0	14.1	-	-
0/2 dolomite	10.0	9.5	22	20.7
2/8 dolomite	10.0	9.5	30	28.3
4/8 ceramics	15.0	14.2	-	-
8/11 dolomite	25.0	23.6	20	18.9
bitumen 50/70	-	5.8	-	5.8
TOTAL	100	100	100	100

The contact angle (CA) characterizing the liquid drop was measured on a research stand, comprising a camera used for capturing the image of a drop put onto surface of a sample. Distilled water wetting angles θ_w , which correspond to the surface coatings, were measured with a liquid characterized by known total SFE values (γ_s). The constant volumes of liquid drops approximated 2 mm³ and were applied onto the sample surface via a micropipette. A profilometer determined the percentage share of different surface. Three types of surface were distinguished in the sample – smooth, porous, very porous based on the observation under an optical microscope. Six drops were applied onto each kind of surface, given the surface porosity of the material. The measurements were conducted at the temperature approximating 22.5°C at the moment of applying a drop.

Neumann model, which constitutes one of the most common methods of calculating SFE, was used in order to determine this parameter [1, 8, 12]. The employed equation was as follows [13]:

$$\cos \theta_w = \left[e^{-0.000125(\gamma_s - \gamma_w)^2} 2 \sqrt{\frac{\gamma_s}{\gamma_w} - 1} \right] \quad (1)$$

where: γ_s – total SFE, γ_w – SFE of water = 72.8 (mJ·mm⁻²), θ_w – water contact angle.

The surface roughness was determined by means of a profilometer -T8000 RC120-400 device by T8000 RC120-140. Scanning electron microscopy SEM (Quanta FEG 250 microscope) was employed to determine the structure of aggregates and mineral-asphalt mixtures.

3. Results and discussion

The results of mineral asphalt mixture density and bulk density are presented in Table 3.

The results of the analysis of mineral asphalt mixture density were nearly identical for all types of specimens, both for the ones consisting of ceramic aggregates, as well as the ones that were produced entirely from traditional dolomite aggregates. The discrepancies arising from different types of aggregates were not higher than 4%. The exactly same conclusions can be drawn after the analysis of the results of bulk density test.

Table 3. Density and bulk density of mineral-asphalt mixtures.

	Density of mineral asphalt mixture (g/cm ³)	Bulk density of specimens(g/cm ³)
WC-1	2.419	2.369
WC-2	2.502	2.460

Figure 1 presents the microstructure of dolomite and ceramic aggregates.

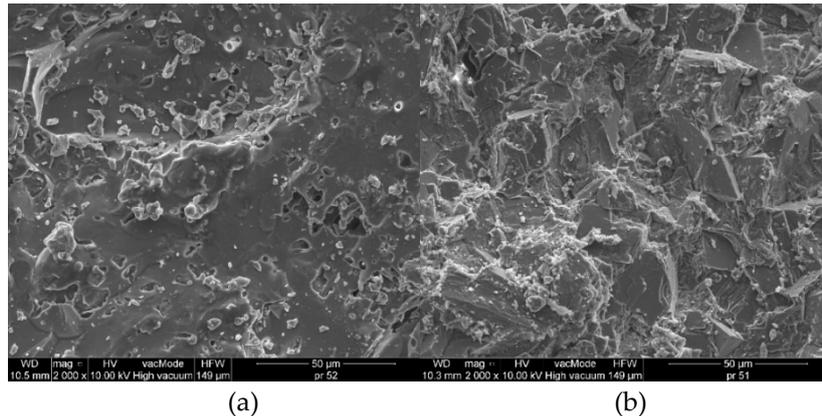


Figure 1. Microstructure of aggregates used: (a) ceramic aggregate; (b) dolomite aggregate (x2000).

Figure 2 presents the microstructure of mineral-asphalt mixture WC-1.

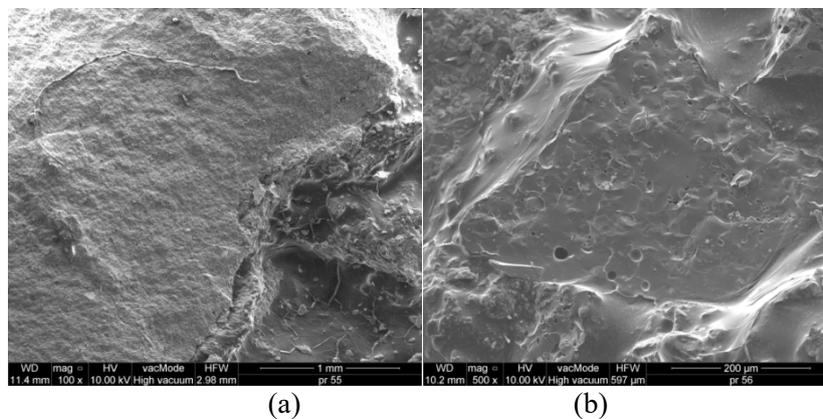


Figure 2. Microstructure of mineral-asphalt mixture: (a) WC-2; (b) WC-1.

Contact angle (CA) and surface free energy (SFE) constitute other parameters defining the wettability of a material [1, 8, 14]. Figure 3 presents exemplary photos of CA water measurements of WC-2 mineral-asphalt mixtures on three different surfaces. SFE of all analyzed bituminous mixes was calculated by means of Neumann's method on the basis of CA measurement.

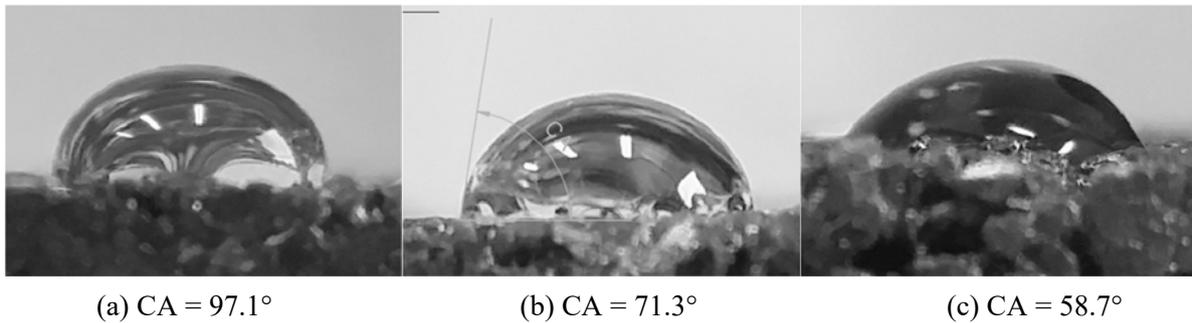


Figure 3. Contact angle of a water drop in WC-2 mineral-asphalt mixtures: (a) smooth surface; (b) porous surface; (c) very porous surface.

Table 4 presents the CA of water measured on each mineral-asphalt mixture in six points with different surface porosity and SFE calculated on its basis. Three types of sample surfaces were defined on the basis of maximum peak-to-valley height S_t (Table 4). S_t have been defined on the basis of the EN15178N standard [15]. Using the obtained data, the weighted average SFE of the specific mixture was calculated.

Table 4. Roughness, CA and SFE of analyzed mineral-asphalt mixtures.

	Unit	WC-1			WC-2		
		smooth surface	porous surface	very porous surface	smooth surface	porous surface	very porous surface
S_t	(%)	34	41	25	30	42	28
	(μm)	280	302	442	203	297	398
	weighted average (μm)	329.52			297.08		
CA	($^\circ$)	78.3	64.9	54.1	96.3	69.4	59.6
	weighted average ($^\circ$)	66.75			74.73		
SFE	($\text{mJ}\cdot\text{m}^{-2}$)	36.59	44.90	51.40	25.33	42.13	48.06
	weighted average ($\text{mJ}\cdot\text{m}^{-2}$)	43.70			38.75		

It can be seen that in both mixtures the porous surface is dominant (41-42%). It should be noted that the smooth surface in both mixtures is different, as shown by the CA measurement. In the WC-2 mixture it is 18.7% higher than in WC-1. The smallest S_t can also be seen in the case of WC-2 smooth surface. The very porous surface of WC-1 are characterized by the greatest roughness which is 442 μm . The weighted average S_t of WC-1 is 10% higher than S_t of mixture WC-2. The obtained results indicate that the values of CA depends on the type of aggregate used in mixtures and smoothness of mineral-asphalt mixtures surface. The results of CA measurements proved that all CA for mineral-asphalt mixtures with dolomite aggregate were higher than the contact angles for mineral-asphalt mixtures with dolomite and ceramic aggregate. The highest contact angle was noticed for the bituminous mixture with dolomite aggregate (WC-2) on a smooth surface and it reached 96.3 $^\circ$. The smallest CA with water was obtained by mineral-asphalt mixture with dolomite and recycled ceramic aggregate on a rough surface, equalling 54.1 $^\circ$. Hence, the total SFE for mineral-asphalt mixtures with dolomite and recycled ceramic aggregate were higher about 11% than SFE for WC-2. The highest SFE was noticed for the bituminous mixture with dolomite and recycled ceramic aggregate (WC-1) on a very porous surface and it was 51.40 $\text{mJ}\cdot\text{m}^{-2}$. The smallest SFE was obtained by WC-2 on a smooth surface and it was 25.33 $\text{mJ}\cdot\text{m}^{-2}$. This is due to physical characteristics of this aggregate, higher WC-1 porosity and absorbability. The correlation between the maximum peak-to-valley height S_t and SFE of WC-1 mineral-asphalt mixtures is shown in Figure 4.

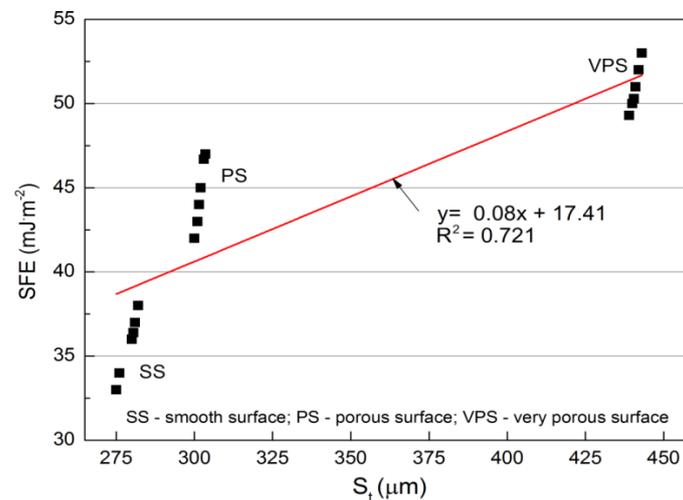


Figure 4. Correlation between maximum peak-to-valley height S_t and SFE of WC-1.

It can be noticed that there is a close correlation between these parameters. The linear function allows to obtain a good coefficient of determination R^2 , equal to 0.721. SFE is the largest for VPS and significantly different from the other two types of surfaces (SS and PS). These correlations mainly stem from changes in the CA of mineral-asphalt mixtures. This is because porosity is strictly connected with absorptivity, CA and SFE.

The characteristics of surface properties, especially SFE, are considered important parameters required for understanding the mechanisms of surface phenomena [1, 8, 12, 14]. Surface free energy is the result of attraction between the molecules in the surface layer and volume of a material [14].

4. Conclusions

The work analysed the physical wettability, surface free energy as well as the microstructure characterizing the mineral-asphalt mixtures with dolomite and ceramic aggregates.

On the basis of the analysis of research, the following conclusions were drawn:

- The smoothness of the surface changes the wetting and adhesion properties of mineral-asphalt mixtures.
- The values of density and bulk density tests of mineral asphalt mixture range within standard requirements and have no significant effect on wettability.
- The smallest contact angle with water was obtained by mineral-asphalt mixture with dolomite and recycled ceramic aggregate on very porous surface. This is due to physical characteristics of this aggregate.
- The smallest SFE was obtained by WC-2 on smooth surface and it was $25.33 \text{ mJ}\cdot\text{m}^{-2}$. That causes the total SFE for mineral-asphalt mixtures with dolomite and recycled ceramic aggregate were higher about 11% than SFE for WC-2. Ceramic aggregate is characterized by high absorbability. This indicates an increased wettability and increased adhesion properties.
- The high level of roughness and good adhesion between the ceramic and dolomite aggregate and asphalt were confirmed by SEM images. The asphalt has very good bonding with the aggregate, there were no micro-cracks or micro-fractures.

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