Microstructural and rheological analysis of fillers and asphalt mastics

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Abstract. Pavements are made of different grades of mineral aggregates and organic binder. The aggregates are sorted in different sizes and different amount which are mixed together with bitumen. The finest mineral fraction (d<0.063 mm) is called filler. This component has an important role in asphalt mixture - it fills the gaps between the aggregates and if mixed with bitumen (which is called asphalt mastics) it sticks the larger particles together. Particle size, microstructure and surface properties of fillers highly affect the cohesion with bitumen, therefore the aim of our research was to investigate the microstructure of mineral fillers (limestone, dolomite) which are used in Hungarian road constructions with the use of different techniques (particle size distribution, scanning electronmicroscopy tests, mercury intrusion porosimetry, BET specific surface tests, determination of hydrophobicity). After the tests of fillers, asphalt mastics were prepared and rheological examinations were obtained. These examinations served to observe the interaction and the effect of fillers. The stiffening effect of fillers and the causes of rutting were also investigated. Based on our results, it can be stated that particle size, hydrophobic properties and the amount of fillers highly affect the rheological properties of mastics.

1. Introduction

Asphalt mixtures are world-wide used pavement materials. They consist of mineral aggregates in different particle sizes and bitumen, as binding material [1]. One of the most important components of asphalt are mineral fillers (d<0.063 mm). The mixture of bitumen and fine mineral particles generates asphalt mastic which is the main bonding phase of asphalt mixture. It affects both the cohesion between coarser particles, which carry capacity to a great extent, and the strength and stiffness of pavement [2, 3, 4, 5, 6].

Nowadays, not only international researches [7, 8, 9] but also Hungarian projects deal with the improvement of pavement performance. Significant results were achieved with the use of different alternative aggregates and other fibre-based asphalt modifiers [10, 11, 12, 13]. Since the performance of pavements highly depend on environmental circumstances (mainly temperature) and on traffic load, it is also important to examine the rheological properties [14, 15].

A fundamental point of the relation formed with bitumen is the mineral origin of the filler. The most widespread used filler is limestone and Hungary has rich and good quality mineral resources of it. Numerous researches have dealt with the investigations of mineral fillers and asphalt mastics to reveal the contact mechanisms between mineral aggregates and bitumen [16, 17, 18]. Our current research tried to widen the knowledge in this topic. As the strength of interaction between bitumen and filler depends
on the properties of components, the Authors have divided the examinations into two parts; analysis of raw materials (filler, bitumen) and analysis of asphalt mastics.

Considering the above mentioned, the aims of this research were the followings:

- complex testing procedures (X-ray powder diffraction, scanning electronmicroscopy, BET specific surface tests, mercury intrusion porosimetry, determination of hydrophilic coefficient) were done on mineral fillers.
- with the use of fillers, asphalt mastic mixtures were created in which effect mechanism of type, particle size and quantity of fillers (volume fraction) can be observed at the same time. Rheological tests were made on the mastics in high temperature ranges in order to describe the behaviour of asphalt pavements in summer.
- summarizing the above mentioned: the aim of this research was to observe rutting, the typical defect of pavements with the use of different mineral fillers.

2. Materials and methodology

2.1. Sample preparation

Two types of mineral materials were tested during the research, which originate from Hungary (limestone /Mexikővölgy/ and dolomite /Pilisvörösvár/). The following sample preparation process were done on mineral fillers: units of mineral materials that are smaller than a given particle size (d<0.063 mm and d<0.045 mm) were created using standard sieves. The fractions were then dried to weight-constancy in a drying chamber. After the samples were cooled down, they were hermetically sealed in containers to avoid moisture uptake until further investigation. Dolomite was supplied in two different particle size ranges (d<0.3 mm, and d<0.045 mm, respectively) which were previously fractioned by the manufacturer.

2.2. Testing procedures

Determination of particle size distribution of fractioned fillers were made with Horiba LA-950V2 instrument. The tests were done by using wet method, therefore to dispergate mineral fillers sodium-pyrophosphate and ultrasonic treatment was also used.

For morphological tests Carl Zeiss EVO MA10 scanning electron microscope (SEM) was used. Micrographs were taken in different magnifications for further observation. Morphology and geometrical features of fillers were observed with this technique.

Specific surface area of the fillers (by BET-method) were determined by nitrogen adsorption method, using TriStar 3000 instrument (manufactured by Micromeritics). In order to determine the pore structure and pore size distribution within the mineral material mercury intrusion porosimetry (MIP) was used by PASCAL 140 and PASCAL 440 instruments (manufactured by Thermo Scientific).

Hydrophilic coefficients of fillers were determined by sedimentation method. The test procedure was described elsewhere [18].

During the research asphalt mastic samples were prepared with the use of mineral fillers and standard bitumen (Százhalombatta) with penetration grade 50/70. The ratios of filler to mastics on a volumetric base (i.e. filler volume/mastics volume; F/M ratio) were selected at 5%, 13% and 20%. Mineral fillers were mixed with bitumen in a mixer in which temperature was kept at 160 °C and mixing speed was 500 rpm.

Haake RheoStress RS80 dynamic shear rheometer with a standard 25 mm diameter parallel plate testing geometry was used to reveal the rheological properties of mastics in the linear viscoelastic region. Considering the particle size of mineral fillers, gap size of rheometer was set to 1.5 mm. Rheological tests were performed between 60 °C-135 °C considering the pavement temperature in summer and paving temperatures. During the research program flow and viscosity curves, master curves, as well as creep-recovery curves were determined.
3. Results and discussion

3.1. Test results of mineral fillers

Table 1. contains all the test results performed on mineral fillers. It was proved by the results of XRD tests that as regards to their mineral composition, fillers are pure materials, free of contamination. Limestone filler contains only CaCO3, while dolomite contains MgCa(CO3)2.

| Material property   | unit | Limestone d<0.045 mm | d<0.063 mm | Dolomite mm d<0.063 mm |
|---------------------|------|----------------------|------------|------------------------|
| Mineral composition | wt%  | 100 % CaCO3          | 100 % MgCa(CO3)2 |
| Bulk density        | gcm$^{-3}$ | 2.717              | 2.842       |
| BET specific surface area | m$^2$g$^{-1}$ | 1.11               | 1.02        |
| Hydrophilic coefficient | -     | 0.74                | 0.76        |
| Average pore diameter | m     | 2.04                | 2.47        |
| Median pore diameter  | m     | 3.78                | 3.80        |

Bulk density of fillers was also determined by pycnometer method. The determination of density was important to create asphalt mastic mixtures. It can be concluded that dolomite has a higher bulk density value.

From the minerals available for the Authors, fractions of different particle sizes were formed. Having defined their particle size distribution it was found that these mineral materials can be characterized as polydisperse systems and they contain fine and coarse particles in different quantity by fraction.

Fig. 1. well illustrates the differences of PSD between the mineral materials. Both fractions of limestone contain much more fine particles (typically particles below 10 microns) than dolomite, which contains quantitatively more of bigger particles. In dolomite (d<0.063mm) there are less fine (d<10 microns) particles. However, in the d<0.045 mm fraction of dolomite the presence of fine particles was highly significant.

During the research BET specific surface area were also determined. It was found that the fractions of fillers, except the coarser dolomite fraction, have a relatively low BET value (~ 1 m$^2$g$^{-1}$), which is favourable in asphalt technology in the viewpoint of bitumen consumption.

Hydrophilic coefficient of fillers were also determined. It can be concluded that all of the fractions are hydrophobic because their hydrophilic coefficients are under 1. As carbonated minerals can form a better
contact with bitumen, the use of these fillers are highly favourable.

Pore size distribution, pore diameters were examined by mercury intrusion porosimetry (MIP). The results shows that the average pore diameter of fillers are about 2-3 μm. The results indicate that in coarser particles there are bigger pores. If median pore diameters are inspected, pore diameter of dolomite (d<0.063 mm) has the highest value. This phenomena was also observed later on during scanning electronmicroscopy studies.

Fig. 2. shows the microstructures of fillers (magnification=200X). The SEM micrographs confirm the results of particle size distribution tests. Both of the fillers can be characterized as a polydisperse system. As it can be seen, the larger fraction of dolomite does not contain much fine particles.

Figure 2. Morphology of fillers

3.2. Rheological test results of asphalt mastics

The behaviour of asphalt pavements depend on the type of loading as well as on temperature [1, 14, 20]. Therefore, pavements are considered as viscoelastic material systems which means that viscous and elastic properties are simultaneously present. It is possible to study the properties of binder-and-asphalt-mixtures under linear viscoelastic circumstances and to reveal the relationships between them [1]. Because of the page limitation of this article, the following diagrams are just examples of the whole research results. On the forthcoming figures asphalt mastics (made with limestone and dolomite fillers in different particle size ranges /d<0.045mm and 0.063 mm/ with F/M ratio of 20%) are shown. Former research results were published elsewhere [22, 23].

During rheological investigations creep-recovery tests were done on fillers. Testing conditions were:
T=60°C and t=1 Pa. Using these parameters all of the tests were made in the linear viscoelastic regime. (Abbreviations on the diagrams are: LS=limestone; D=dolomite; 45μm/63μm=particle size ranges of fillers; 025=F/M ratio).

Figure 3. Flow curves of asphalt mastics at 60 °C and 135 °C

Figure 3. shows the creep-recovery curves of asphalt mastics. It can be concluded that with the use of fillers the strain of binder material can be reduced. The pure bitumen has the highest deformation during loading, and at the same time the coarser fraction of fillers will produce the lowest strain in material structure. After unloading in the recovery phase the lowest permanent deformation was produced by limestone.

To examine the flow phenomena of asphalt mastics, flow curves and viscosity curves were determined. At the lowest testing temperature (summer conditions), because of the high viscosity of mastics, shear rate was set up to 20 s⁻¹. At elevated testing temperatures (compacting temperature) shear rate region was extended up to 200 s⁻¹. The determined flow curves of mastics at 60 °C and 135 °C are shown in Figure 4.

Figure 4. Flow curves of asphalt mastics at 60° C and 135° C

As bitumen and asphalt mastics have yield stress, e.g. the mixtures are pseudoplastic and can be described at lower testing temperature with Herschel-Bulkley model. At higher testing temperatures flow phenomena were changed. Newtonian flows were observed above the yield stress, therefore the mixtures behave as Bingham materials.

Dynamic oscillatory tests were also obtained on mastics. During these tests frequency ranges were chosen 0.1 Hz-10 Hz, while temperature was changed by 15°C. Dynamic parameters (storage and loss modulus, complex modulus, phase angle and loss tangent) were determined and using the WLF-equation master curves of mastics were constructed. Reference temperature were chosen at 60°C. Figure 5. shows the complex modulus and phase angle master curves of mastics.
The master curves show well the effect of particle size and quality of fillers on the complex modulus (properly speaking the stiffness). It can be concluded that limestone can create a stronger contact with bitumen than dolomite. Coarser particles increased the modulus, therefore using these particle sized fillers elastic properties can also increase. On closer examination of phase angle master curves the results prove the above mentioned. Limestone, especially the coarser fraction, can improve the elastic behaviour of mastics much better than dolomite. However, using both fillers phase angle will decrease, therefore the elastic properties of mastics will increase. The usage of these mineral materials as fillers can decrease rutting of pavements.

4. Conclusions

During this research work two types of fine particle mineral materials were tested as asphalt fillers. Examinations of raw materials as well as asphalt mastics were made by different techniques.

Having defined their particle size distribution it was found that these mineral materials can be characterized as polydisperse systems and they contain fine and coarse particles in different quantity by fraction.

By material structure test the Authors have observed the morphological features of fillers. The form of particles is diversified, their surface is broken up by sharp borders due to comminution processes, which increase the internal friction of the mineral skeleton and pavement. Polydispersity of mineral materials ensures good space filling and through this greater compactness and strength for asphalt mixtures.

During the examination of the material structure signs of minimal porosity and small specific surface area was observed. Porosimetry tests showed that coarser particles contain bigger pores within the material structure.

It was proved that the particle size distribution of the fractions as well as the quantity of fine and coarse particles affect the material features in each case. Presence of fines result in the increase of specific surface area but at the same time decrease the value of the hydrophilic coefficient, improving the bitumen stabilizing ability of mineral materials.

By the use of fillers the Authors have created asphalt mastic mixtures in which effect mechanism of type, particle size and quantity of fillers (volume fraction) can be observed at the same time. Rheological tests on the mastics were made with which the behaviour of asphalt pavements in summer can be described. With the measuring methods used, the purpose was to observe rutting, the typical defect of pavements.

During the analysis of creep-recovery features the behaviour of mastics were investigated. In view of the results it was also stated that the coarse particles in mastics increase the elasticity of mixtures in each case and thus decrease strain that is developed to the effect of load and also the amount of deformation remaining from recovery. It was also proved that during the use of limestone minor deformations developed which relates to the fact that limestone is able to create stronger relation with the binder.

To examine the flow phenomena occurring during the operational use of pavements in summer and the compacting of asphalt mixtures the real flow curves and viscosity curves of mastics were...
determined. As mixtures have yield stress, besides the viscoelastic nature of mixtures, there is also plasticity to certain extent in the material system. Having this in mind the mixtures were characterized with two rheological models in the testing temperature ranges. It was proved that at lower testing temperatures mastics behave as pseudoplastic materials and they could be described with Herschel-Bulkley model. At higher testing temperature the materials behave as Bingham materials. With measuring results it was reinforced that with the increase of the amount and particle size of fillers pseudoplastic nature is strengthened, while at the highest testing temperature - which is in fact the compacting temperature of asphalt pavements - mastics can be characterized as Bingham materials one and all.

With dynamic tests the dependence of asphalt mastics particle size and quantity of fillers the elastic properties will dominate and as a consequence stiffening effect will increase. It was stated that due to the strong interaction between limestone and bitumen stiffness will be greater than during the use of dolomite. All in all, we can say that the use of the observed mineral materials - especially limestone - as asphalt fillers is advantageous in any case as due to their favourable features the stiffness of pavements at high traffic temperature can be improved to a great extent, their resistance to deformation can be increased and finally the possibility of rutting formation can be decreased.

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