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# Investigation of nano ulexite mineral effects on mechanical behaviour of warm mix asphalt pavements

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Research paper

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## Investigation of nano ulexite mineral effects on mechanical behaviour of warm mix asphalt pavements

The research presented in the paper shows that further investigations on additives used in the warm mix asphalt technology are needed. It was observed that the negative effect of adhesion loss in asphalt mixes produced by warm process can be reduced by adding ulexite mineral nano particles to a commercial additive. The Marshall stability, Indirect tensile strength modulus, and moisture susceptibility, were tested for this purpose. Based on the analysis of results, it can be seen that the WMA mixture production temperature can additionally be reduced, and that lower compaction energy is needed during placement of such mixtures, which results in energy savings.

### Key words:

warm mix asphalts, ulexite mineral, Marshall stability, moisture susceptibility, tensile strength

Prethodno priopćenje

**Tuba Kütük-Sert, Resul Ekrem Günbey**

## Ispitivanje utjecaja nano čestica minerala uleksita na mehaničko ponašanje toplih asfaltnih mješavina

U radu je prikazano istraživanje pokazalo je da su potrebna daljnja ispitivanja aditiva u tehnologiji proizvodnje toplih asfaltnih mješavina. Uočeno je da se negativni učinak gubitka adhezije u asfaltnim mješavinama proizvedenim toplim postupkom može smanjiti dodatkom nanočestica minerala uleksita komercijalnom aditivu. U tu svrhu provedena ispitivanja stabilnosti po Marshallu, indirektno ispitivanje modula vlačne čvrstoće i ispitivanja osjetljivosti na vlagu. Na temelju analize dobivenih rezultata vidljivo je da se temperatura proizvodnje WMA mješavine može dodatno smanjiti, a prilikom ugradnje takvih mješavina potrebna je manja energija zbijanja, čime se osigurava ušteda energije.

### Ključne riječi:

tople asfaltnje mješavine, mineral uleksit, stabilnost po Marshallu, osjetljivost na vlagu, vlačna čvrstoća

Vorherige Mitteilung

**Tuba Kütük-Sert, Resul Ekrem Günbey**

## Untersuchung des Einflusses von Nanopartikeln des Minerals Ulexit auf das mechanische Verhalten heißer Asphaltmischungen

In der Abhandlung hat die Untersuchung gezeigt, dass weitere Untersuchungen von Zusätzen in der Technologie der Herstellung von heißen Asphaltmischungen erforderlich sind. Festgestellt wurde, dass der negative Effekt des Adhäsionsverlustes in Asphaltmischungen, hergestellt durch ein heißes Verfahren, durch die Zugabe des Minerals Ulexit zum kommerziellen Zusatz verringert werden kann. Zu diesem Zweck wurden Untersuchungen der Stabilität gemäß Marshall, indirekte Untersuchungen des Zugmodells und die Untersuchung auf Feuchtigkeitsempfindlichkeit durchgeführt. Aufgrund der Analyse der erhaltenen Ergebnisse ist ersichtlich, dass die Produktionstemperatur von WMA-Mischungen zusätzlich gesenkt werden kann, und bei Einbau solcher Mischungen ist eine geringere Verdichtungsenergie erforderlich, was Energieeinsparungen gewährleistet.

### Schlüsselwörter:

heiße Asphaltmischungen, Mineral Ulexit, Stabilität nach Marshall, Feuchtigkeitsempfindlichkeit, Zugfestigkeit

## 1. Introduction

Turkey has about 63 % or 803 million tons of the world's boron reserves [1]. Annual production of boron ore in Turkey amounts to about 1.3 million tons. The ulexite used in this study is an important boron mineral. Its formula is  $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$  and it contains 16 moles of water. Ulexite, kernite, probertite, and szaibelyite are commercially significant. However, in commercial terms, ulexite is considered to be the most significant of these minerals [2]. Attempts have been made to overcome the shortage of ulexite mineral in asphalt industry, especially in warm mix asphalt production, where this mineral is very attractive as commercial product and raw material.

Due to mixture properties, such as an increased workability and better compaction, warm mix asphalt pavements have attracted considerable interest in recent years [3]. New technologies have made it possible to decrease the production and application temperatures of asphalt. These technologies allow production of asphalt mixtures at lower temperatures compared to conventional hot mixes, by reducing bitumen viscosity. Warm mix asphalt is a bituminous mixture prepared by a suitable method so as to reduce the bituminous hot mixture temperature by at least 20 - 30 °C, the aim being to save energy and reduce emissions [4].

As the temperature is reduced by 10 °C during preparation of the mixture, while the emissions are reduced by 50 %, it is clear that this not yet widely accepted technology will gain in significance in the future [5]. The idea of using additives to reduce mixing and compaction temperatures in bituminous mixtures was developed in Europe in the early 1990s. Initial experiments focusing on warm asphalt mixtures were carried out in Europe in order to reduce pollution effects, in response to the Kyoto Protocol. An improvement has been noted in the compressibility of asphalt mixtures at low temperatures, and in maintenance or improvement of mechanical properties of warm mix asphalts [6]. In addition, since the mixture can be produced at lower temperatures compared to warm mixing, the bitumen inside it is aging less and is more resistant to thermal and fatigue cracks [7]. Warm mixes are preferred in terms of advantages during construction and for ease of construction, and due to their capability to reduce emissions. Warm mix asphalt technology has been proven to reduce the emissions of odour, fumes and polyaromatic hydrocarbons (PAH) by 30 to 50 percent when compared to conventional bituminous hot mix asphalts [6]. Warm asphalt application is ideal (NCAT) as a means of providing a cleaner working environment for workers employed in road construction. Semi-warm asphalt mixtures produced with low energy result in fuel savings amounting to at least 50 %.

Cases of lack of adhesion and stripping between aggregate and bitumen can be observed as a result of foaming that occurs in the warm mix asphalt technology. In addition, some additives are added due to the long-time asphalt mixture preparation cycle, which causes incompatibility between bitumen and

minerals because of excessive moisture in mineral materials. Appropriate additives have been used to solve this problem [8]. In this study, preference is given to a nano-sized additive. Nano sized materials are used in engineering so as to obtain more stable and durable materials that offer better important properties compared to general ones [9].

Research on this topic has also been conducted on micron- and nano-sized materials, as well as on warm mixture asphalt. Moisture sensitivity of warm mixed asphalt containing nano-sized hydrate lime has also been investigated in literature [10]. The authors of some studies predict that nanofibres exhibiting a uniform distribution within bitumen would play almost an adhesive role between the bitumen and aggregate without any physical effect and would, in other words, improve adhesion [11]. The usability of nano materials in asphalt and bitumen has also been studied [12].

When reduced to nano dimension, the behaviour of the material changes, such as its melting temperature, magnetic properties, and colour. The use of nanotechnology improves various properties of asphalt and bitumen. The adhesion and shear strength of the bitumen modified with nano clay increases and the resistance to deformations improves. Furthermore, the addition of nano clay reduces fatigue at low temperatures. Based on results of the research related to low temperatures, it is considered that nano additives will perform well in warm mixture asphalt concrete.

The performance of asphalt concrete with the addition of nano calcium carbonate has also been studied [13]. It was established that 6 % of nano calcium additive improves dynamic stability of the admixture. The authors of another study emphasized that the application of nanotechnology in civil engineering is fairly new, and tested performance of bituminous mixtures containing 0 %, 0.5 %, 1 % and 1.5 % of carbon nano sized additive [14]. It was revealed that the deformation resistance of the mixtures increased with the addition of nano sized additives.

The alteration of stone mastic asphalt modified with nano  $\text{SiO}_2$  has also been studied [15]. The  $\text{SiO}_2$  mean size was milled to 15 nm. The SBS / Nano  $\text{SiO}_2$  modified mixtures shows higher stability and tensile strength than the control mixture, and the adhesion and cohesion of SBS / Nano  $\text{SiO}_2$  additive mixtures increases.

The use of various nano materials in asphalt pavements was analysed in [16]. In this research on nano clays, it was observed that the asphalt blend increased the shear modulus of the 2 % nano clay additive by 184 %, while improvement in rutting resistance was also observed.

Rheological properties of the warm mix asphalt modified with nano hydrate lime was studied in [17]. The hydrate lime was reduced to 50 nm and 100 nm, and used in this study. Mixtures were prepared by adding 5 %, 10 % and 20 % of the asphalt binder in amounts of nano hydrate lime, and 3 %, 4.5 % and 6 % of the foaming admixture, and tests were conducted to determine cracks in the formation of wheel marks, as well as fatigue cracks and thermal cracks. The researchers have found

that nano clay and carbon micro fibre admixtures improve the moisture sensitivity performance of asphalt mixtures and reduce the moisture damage potential in many situations [18]. It was observed that the use of nanoscale had positive effects on moisture sensitivity. The addition of 1.5 % nano clay and 1.5 % carbon micro fibre additive provides ideal results for an increase in tensile strength.

As is known, warm mixture asphalts are obtained using a number of additives. In a study using various commercial additive products, the repeated creep characteristics of samples were examined, and it was observed that the unused samples show lower creep rates than those used, and that the wheel tracking resistance is higher despite the increase in viscosity. Warm mix asphalts allow workability at low temperatures of asphalt. This is enabled by substances such as chemical admixtures that are liquid at room temperature, zeolite-containing foam admixtures, and wax additives (a kind of chemicals) consisting of long chain hydrocarbons [19]. An interesting aspect of the warm mix asphalt obtained with foamed additives is that the temperature changes of the 3 % water-foamed binder are less sensitive compared to foamed binder with 1 or 2 % of water. The test results show that unmodified and SBS modified asphalt binders differ in foaming [20].

Laboratory performance of sulphur-modified warm mix asphalt has also been analysed. Three different mixtures were prepared: two hot mixes and one warm mix, as shown in [21]. Sulphur modified warm asphalt mixture exhibited excellent performance in terms of tensile strength ratio, as well as good performance with respect to the depth of the wheel track between hot mixtures with and without additives. The use of the recycled asphalt (RAP) additive in warm mixed asphalt was also researched [22]. It was determined that the optimum RAP content to be incorporated into the mixture should not exceed 30 %. In another study investigating the influence of additives on the wheel tracking performance of warm mix asphalt, two different additives with wax and chemical content were used, and the depth of the wheel traces of the coatings in which wax additives were used was found to be lower than in other cases [23]. In the study of the effectiveness of activated carbon in bitumen modification, it was established that viscosity

increased and workability decreased with active carbon modification [24].

The use of boron minerals as additive to asphalt is described in a number of published studies. In these studies the mentioned minerals were used to improve performance properties of asphalt [25]. It was observed that the new boron additive, called CBE, improves aging resistance and low-temperature cracking resistance of asphalt but not cohesion. In another study, properties of asphalt concrete containing boron residues as mineral filler were investigated. It was concluded that the boron residue can be used in asphalt pavements subjected to medium and low-traffic [26].

Based on this background information, boron minerals, abundant in Turkey holding the majority of the world's boron reserves, were added in this study to the foamed warm mixture asphalt at varying ratios in submicron dimensions. Properties such as adhesion and strength, changed with more stable structures obtained by reducing minerals to submicron sizes, are investigated in this research. It is known that adhesion-improving chemicals are often used in order to increase the efficiency of the warm mixture additives. In this study, improvements were made to mechanical properties of the material using only the size reduction of the material, without using chemical additives. This study, in which the use of nano sized boron (ulexite) minerals in warm mix asphalt is evaluated, is unique in literature as to this particular aspect.

## 2. Materials and methods

### 2.1. WMA design

Laboratory test results were analysed to determine whether significant changes can be observed in Warm Mix Asphalt (WMA) produced using different ratios and dimension sizes of ulexite with the same mix design. WMA specimens were prepared with limestone as aggregate, B50/70 bitumen as binder, and ulexite minerals as additives to modify the mix. Mixture calculation was conducted for the wear course Type 1 (AC16 50/70). Table 1 was produced as a reference for checking suitability of physical properties of the mixture, including compaction.

**Table 1. Mix design parameters**

Parameters	Test standard	Result	Specification
Bitumen [%]	TS EN 12697-1	4.6	4.0-7.0
Specific gravity [g/cm <sup>3</sup> ]	TS EN 12697-6	2.43	
Marshall stability [kg]	TS EN 12697-34	1220	Minimalno 900
Voids [%]	TS EN 12697-8	4.0	3-5
Voids filled asphalt [%]	TS EN 12697-8	70.0	65-75
Voids in mineral aggregates (VMA) [%]	TS EN 12697-8	14.05	14-16
Flow [mm]	TS EN 12697-34	3.50	2-4
Filler/bitumen ratio		1.2	Maksimalno 1.5

Table 2. Aggregate test results

Properties	Unit	Test method	Specification	Tert results
Flakiness index	[%]	TS EN 933-3	-	17
Crushing and abrasion resistance	[%]	TS EN 1097-2	max. 30	22
Absorption	[%]	TS EN 1097-6	max. 2.0	0.62
Magnesium sulfate test	[%]	TS EN 1367-2	max. 16	8.8
Stripping resistance	[%]	Nicholson	max. 50	60-70
Coars aggregate density	[g/cm <sup>3</sup> ]	TS EN 1097-6	-	2.71
Fine aggregate density	[g/cm <sup>3</sup> ]	TS EN 1097-6	-	2.68
Filler density	[g/cm <sup>3</sup> ]	TS EN 1097-7	-	2.745

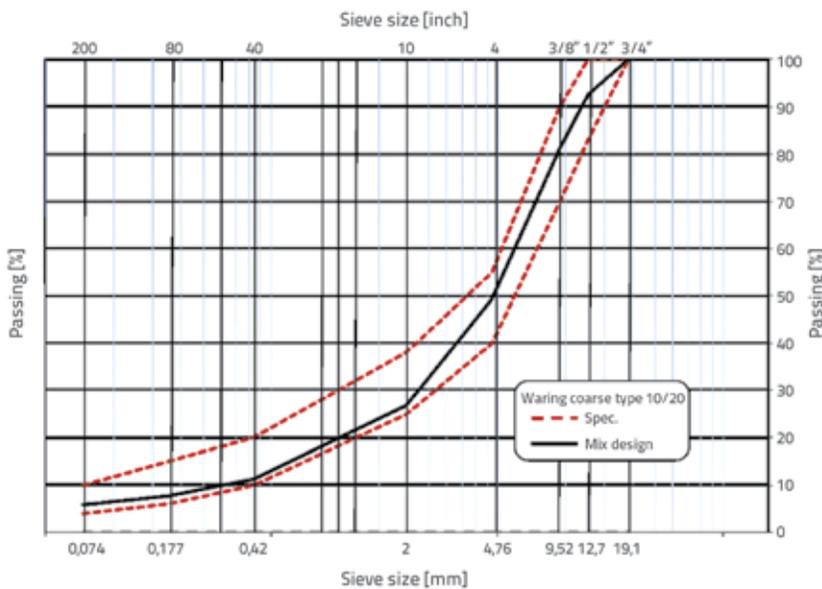


Figure 1. Aggregate gradation curve for WMA

### 2.2. Aggregate analysis

The sieve analysis and the gradation curve of the aggregate used when preparing the bituminous mixture is shown in Figure 1. Some standard tests were applied to indicate physical properties of the aggregate. The objective of these tests applied on the aggregates was to determine the properties of the coarse and

fine limestone aggregate and to decide on their suitability for the mix. The density of the filler was evaluated at 2.745 g/cm<sup>3</sup>. The test results for both the coarse and fine aggregates are shown in Table 2. The gradation chosen for this project was the wearing course Type1 gradation as defined in Turkish Road Authority specification. Aggregate quality and type were chiefly defined to determine the asphalt pavement performance indicators such as friction properties [27].

### 2.3. Characterization of bitumen (B 50/70)

The binder (B 50/70 Bitumen) chosen for this study originated from Turkish Petroleum Refineries. In the binder testing system, binder samples were defined as 50–70 pen (B 50/70).

Standard bitumen tests were carried out on conventional binder samples. In the first group, B 50/70 bitumen samples were tested as control specimens. Standard conventional and modified bitumen tests included: penetration, softening point, Fraass breaking point, flash point, density, kinematic viscosity, and loss on heating. Conventional bitumen test results are shown in Table 3.

Table 3. Binder test results

Properties	Unit	Test method	B 50/70 control
Penetration grade	0.1 mm	TS EN 1426	61.6
Softening point	[°C]	TS EN 1427	49.2
Fraass breaking point	[°C]	TS EN 12593	-12
Flash point	[°C]	TS EN 2592	326
Density	[g/cm <sup>3</sup> ]	TS EN 15326	1.029
Kinematic viscosity	[mm <sup>2</sup> /s]	TS EN 12595	467.5
Loss on heating	[%]	TS EN 12607-2	0.4



Figure 2. Stereo optical microscope image of: a) unmilled (U-3 m) ulexite mineral; b) milled (U-25  $\mu$ )  $\times$  45 magnification

## 2.4. Ulexite mineral specifications and Advera additive

The commercial ulexite mineral (U-3 m) supplied by Eti Mine Works General Management's Bigadic Bor Mine (Eti Mine) is shown in Figure 2a. The U-3 m mineral has a weight percent of  $25.50 \pm 1.50$  for  $B_2O_3$ , which is a merit in the structure. In a planetary high-energy ball mill located at Recep Tayyip Erdogan University, U-3 m mineral was ground based on appropriate milling parameters. Properties of ulexite and examination details are available in other studies [28-30]. The milled ulexite mineral (Fig. 2b) was sieved according to ASTM standard on 25  $\mu$ m (No. 500) and 53  $\mu$ m (No. 270) sieves. Undersize 25  $\mu$ m powder was called U-25  $\mu$  and oversize 53  $\mu$ m powder was called U+53  $\mu$ . The U+53  $\mu$  and U-25  $\mu$  powders have a crystalline size of 25.7 nm and 28.7 nm, respectively. In addition, detailed studies on sieved powders can be found in literature in the context of physics and material engineering.

The Advera utilized to produce foamed WMA is a synthetic zeolite product. It has a very fine white powdered texture, and passes through a 75  $\mu$  (No. 200) sieve. It consists of hydrothermally crystallized framework silicates with voids allowing large cations. The percentage of water retained internally by Advera zeolite is 21 % by mass, and it becomes loose at approximately 100°C. When Advera is mixed into binders, it becomes moist and bubbles can be noted. Volume expansion occurs in the binder, which causes asphalt foam and provides higher machinability and aggregate coverage at low production temperatures. Gradual release of water can provide approximately 7 hours of recyclable processing capability. In this study, Advera was added at the rate of 5 % by weight of asphalt binder.

## 3. Experimental methodology

A laboratory tests were realized with warm mix asphalt (WMA) samples, so as to compare the mixtures (typical dense graded mixtures; Turkish Road Authority, Wearing

Course Type 1 0/20), to determine their properties. The aggregate was heated to about 120-125 °C and the bitumen was heated to 150 °C, so that the approximate mixture temperature was 135 °C, and the mixtures were prepared. The WMA additive Advera (up to 5 % of the bitumen) was added to bitumen just before the mix, and then the ulexite was added to the bitumen, and then mixed with the heated aggregate, thus enabling preparation of mixtures with an optimum bitumen percentage of 4.76 %. The compression was operated by applying 35 pulses to each sample until all samples were provided with 6 % voids according to the design criteria. 5 and 10 % of the bitumen from Ulexite minerals with dimensions of under 25 microns (U-25  $\mu$ ) and over 53 microns (U+53  $\mu$ ) and Advera, 5 % of the bitumen, were added, and 6 different designs, including 4 pieces mixed and 1 piece pure reference, and 1 piece Advera mixed reference, which was up to 5 % of bitumen, were prepared. As to the mixing procedure, Advera was added after the mixing of aggregate and bitumen started and, immediately thereafter, the ulexite was added to the mix.

### 3.1. Bending Beam Rheometer (BBR) tests

The Bending Beam Rheometer (BBR) experiment was carried out for the purpose of observing low temperature cracks, also called thermal cracks, which are caused by climate and environmental conditions but are not dependent on load in flexible pavements constructed in cold climate regions.

This experiment is used to measure how much the asphalt binder will creep or deflect at a certain temperature and at constant load, the aim being to determine elastic behaviour at lowest temperatures that the asphalt pavement can encounter. Since this experiment can also be carried out with RTFOT and PAV tests on aged binders, it is also possible to detect the change in binders over time. In addition, hardness behaviour of the binder at high and low temperatures is evaluated and DSR and BBR experiments are made in a wide temperature range. In the experiment,

a constant single force is applied to the stringer-shaped asphalt stick with a standard size of 12.5 x 125 x 6.25 mm; the hardness and ratio of creep are calculated by measuring the deflection formed in the middle of the stick during the experiment. The loading during the experiment represents the thermal stresses that the pavement is exposed to slowly at very low temperatures.

### 3.2. Marshall stability tests

Marshall Stability tests of WMA were performed on compacted specimens to determine the stability and flow values of the samples. Laboratory test results were evaluated, using the stability correlation ratio values, if the specimen's thickness did not amount to exactly 63.5 mm. The Marshall stability was conducted to determine the breaking force of specimen, and the specimen's diametrical deformation at failure was calculated as flow. The purpose of the Marshall test is to determine the stability of the sample at the exact time when it breaks under pressure. A commonly known test apparatus which breaks the asphalt sample axially was used as the test apparatus. The maximum bulk specific gravity of asphalt mixtures was also determined according to EN 12697. The air voids content of the mixtures (Va), the voids in mineral aggregates (VMA), and the voids filled with asphalt (VFA), were determined by equations presented in the Asphalt Institute Manual.

### 3.3. Moisture susceptibility analyses

Moisture susceptibility of mixtures is important to determine its behaviour or susceptibility to damage under weather conditions. The presence of water in asphalt mixtures is an unwanted condition that is detrimental to pavement structure, as it can cause deformation between the binder and the aggregates. Sample preparation, conditioning, and test steps for the water sensitivity test, were carried out according to TS EN12697-12 ITR. Three conditioned asphalt briquettes and three unconditioned asphalt briquettes were prepared for each situation. For conditioning, the samples were kept in water for 72 hours at 40 °C, and then for 2 hours at 25 °C. For unconditioned dry samples, the waiting operation was performed for 2 hours at 25 °C. After this step, conditioned and unconditioned specimens were fractured in a specially grounded Marshall test device to determine their strength. An indirect tensile fixture was mounted on this Marshall device for measuring purposes.

### 3.4. Indirect tensile strength modulus (ITSM) tests

The stiffness modulus is considered to be a very important performance feature of road and surface layers. The ITSM

test identified with BS DD213 is a test that does not harm the sample and is known as a potential tool for measuring this parameter. The test is carried out using the Universal Testing Machine (UTM-5P). The samples prepared for the test are placed in the loading apparatus for uniaxial loading, and the sensors are connected. The load increase time is determined by considering vehicle speeds. The estimated Poisson ratio of the mixture (0.35), target deformation (mean 4 µm), and load increase times, are entered as data into the computer, and the test is started. The test is based on 5 pulses, which are at 0 °C, 10 °C and 20 °C, with a period of 3000 ms, and a loading time of 126 ms, with controlled deformation.

## 4. Results and discussions

### 4.1. Bending beam rheometer (BBR) tests

According to creep ratios shown in Figure 3, it can be seen that all nano ulexite added to WMA samples provides a minimum value of 0.300 at -6 °C. Moreover, the criterion has been achieved by carrying the value of creep ratio in reference sample above the value of original bitumen with the nano ulexite addition, while it is below the minimum value. This situation indicates that the nano ulexite additive material gives resistance to the WMA by reducing tendency to crack at low temperatures. The greatest effect has been achieved with the 5 % U-25 µ additive content. When the stiffness values are examined in the same way, it can be seen that the prepared samples at all additive contents satisfy the criterion by remaining below the stiffness criterion value of maximum 300 MPa.

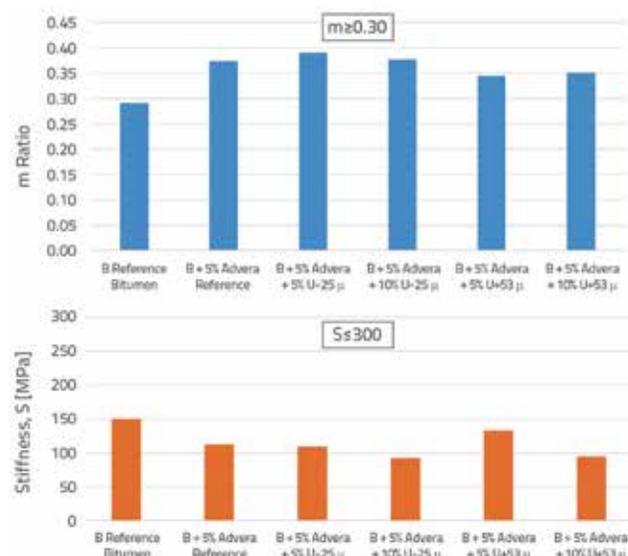


Figure 3. Stiffness and m ratio graphics related to BBR test

Table 4. Va, VMA and VFA values for reference and modified binders

Mixture properties	Ref. bitumen specificatios	Modified binder type				
		B + 5 % Adv	B + 5 % Adv + 5 % U-25 $\mu$	B + 5 % Adv + 10 % U-25 $\mu$	B + 5 % Adv + 5 % U+ 53 $\mu$	B + 5 % Adv + 10 % U+53 $\mu$
Air voids (Va), [%]	4.00	4.66	4.35	3.88	2.21	5.14
Voids in the mineral aggregate (VMA), [%]	14.05	15.05	14.77	14.35	12.86	14.80
Voids filled with asphalt (VFA), [%]	70.00	69.01	70.54	72.96	82.79	65.26

## 4.2. Marshall test results

The Va, VMA, and VFA values of asphalt mixtures are shown in Table 4. Voids in mineral aggregates (VMA) and voids filled with asphalt (VFA) values obtained by Marshall tests have a great importance for the performance of the mixtures. Compared with the reference bituminous mixture, only the Advera, involving mixtures produced without ulexite mixture, have more air voids. In the case of ulexite mixtures, ulexite with + 53  $\mu$  size has a variable table depending on the additive ratio of the added mixtures. In the case of addition of ulexite minerals with a size of -25  $\mu$ , the results of the reference bituminous mixture were obtained. The use of a small amount (5 %) of additives in -25  $\mu$  sized ulexite involving mixtures containing nano sizes increased the air void content, while the use of the excess (10 %) of additive in + 53  $\mu$  ulexite involving mixtures increased the air void content. In terms of their structural properties, ulexite minerals can exhibit foaming properties. Foaming in WMA is important because it helps reduce the temperature, while increasing the workability. In this context, it is very important for WMA that ulexite can exhibit this feature. This feature can be explained by the observation of higher voids in mixtures containing B + 5 % Advera + 10 % U+53  $\mu$  sized admixtures and a high specific area of micron sized particles when examining 25  $\mu$  and 53  $\mu$  ulexite mineral mixtures.

In general, the maximum 6 % void content obtained in all blends indicates that the results are within acceptable limits [31].

Again, as can be seen in Table 4, VMA and VFA values are also examined as the number of additives increases. B + 5 % Advera

+ 5 % U-25  $\mu$  and B + 5 % Advera + 10 % U-25  $\mu$  show almost similar results within themselves, but the results also vary in the U+53  $\mu$  mineral depending on the 5 % and 10 % rates. The lowest VMA and highest VFA values were obtained in admixture with B + 5 % Advera + 5 % U+53  $\mu$  mineral. According to the "Turkish Highway Specification Limits" for binder course, the range of VFA and VMA values are 60 % to 75 % and 13 % to 15 %, respectively. According to evaluation results, it can be said that experimental data are within limits set in specification.

When the Marshall Stability values are examined, it appears that stabilization improves by increasing the amount of ulexite. The highest stability value was obtained in the mixture of B + 5 % Advera + 5 % U+53  $\mu$ . The stability of the mixture obtained with this addition was by 29 % better than the reference bitumen mixture and only by 13 % better than the 5 % admixture. At the 10 % ulexite addition, the same stability value was obtained for both sizes (lower than 25  $\mu$ , higher than 53  $\mu$ ). From here, it can be said that the size of the ulexite involved is also important. Thus, the contribution of 5 % was better than that of 10 %, and the same was observed in the formation of voids. This indicates that the optimum amount of ulexite mineral is almost close to the optimum amount of bitumen, which is 4.76 %.

When the flow values are considered, it can be seen that the highest flow is obtained in the mixture of B + 5 % Advera + 5 % U+53  $\mu$ . This shows that the resulting mixture has a more flexible structure. Although B + 5 % Advera + 5 % U+53  $\mu$  mixture has the highest flow value, and the stability value of this mixture also increased. Since the stability increased by about 13 % and the yield increased by 24.84 %, the Marshall Quotient value was

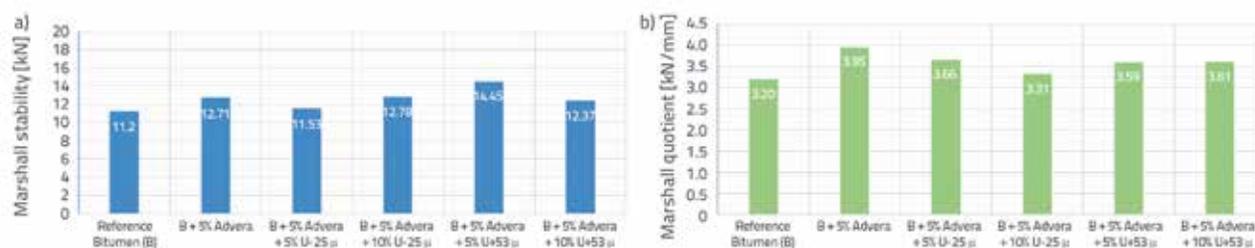


Figure 4. a) Marshall stability; b) Marshall quotient values of tests

also preserved. Again, in the study, the flow values obtained with all types of additives are within specification limits [31]. The ratio of Marshall Stability to flow is defined as Marshall Quotient (MQ). It is the value determined separately for each sample and an indicator of the stiffness of mixtures. In general, MQ values are used as a measure of the material's resistance to shear stresses, permanent deformation and resistance against rutting [32]. Higher MQ values are indicative of higher resistance to creep deformation, the ability of the applied load to spread over a larger area, and high stiffness [33]. At the same time, resistance to continuous deformation is defined. In this study, U+53 μ minerals, both 5 % and 10 % ratios, have good results compared to U-25 μ minerals. Marshall ratio was preserved in the additions of both additives (Figure 4a and 4b), although the highest Marshall stability value was obtained from B + 5 % Advera + 5 % U+53 μ mixture.

### 4.3. Marshall moisture susceptibility test results

In the Moisture Susceptibility analysis, the ITS values were calculated with and without conditioning and Equation 1 was obtained. The indirect tensile resistance ratio of unconditioned samples (ITS dry) and conditioned samples (ITS wet) is calculated according to the following equation:

$$ITSR = ITS_m / ITS_s \tag{1}$$

where:

ITS<sub>m</sub> - the average indirect tensile resistance of conditioned samples [kPa]

ITS<sub>s</sub> - the average indirect tensile resistance of unconditioned samples [kPa].

The indirect tensile strengths of conditioned samples (wet) are divided by the indirect tensile strengths of unconditioned (dry) samples and indirect tensile strength ratios (TSR), which are a measure of moisture sensitivity, are thus determined.

It is remarkable that the moisture susceptibility in mixtures prepared only with boron minerals, without Advera contribution, gets close values. More precisely, conditioning does not significantly affect the moisture susceptibility of the samples, and the strength loss is not considerable. The loss of strength with conditioning is about 15 % for reference samples, but it amounts to only about 3-4 % for ulexite added samples. This is an ideal behaviour of the ulexite additive. In particular, a series of experiments involving ulexite only was carried out in order to observe solely the behaviour of the ulexite mineral but, in this case, without Advera. In conclusion, this result has been achieved. This is the reason for preference for asphalt pavements in continually rainy climates [34]. However, even if the tensile strength increases slightly in Advera added samples, the strength reduces significantly by conditioning.

When Table 5 is examined, it can be noticed that the amounts of 5 % and 10 % of the U-25 μ admixture, and 5 % and 10 % of

the U+53 μ admixture, bring about an increase in the indirect tensile stress ratio values. It was observed that this reduces the indirect tensile strength to some extent. This indicates that an ideal ratio of ulexite addition for coarse or fine sizes is 5 % by weight of the amount of asphalt cement.

Although ITS values are generally reduced in mixtures made with boron minerals, the resulting loss of strength due to conditioning is not significant. This result reflects the fact that the contribution of nano boron minerals can provide more consistent results on stripping resistance. In the experiments with Advera, which is a warm mix asphalt additive, it was observed that ITS values were almost close. However, ITSR results were found to be well below the acceptable limit (Figure 5).

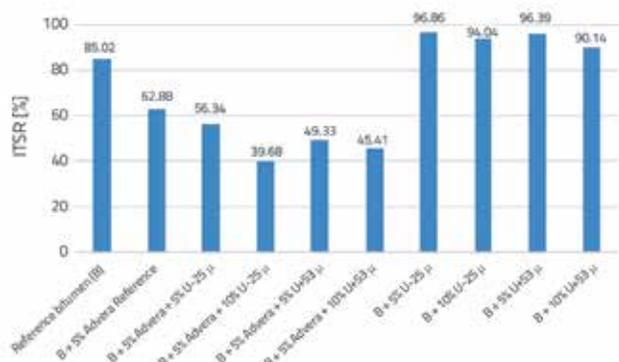


Figure 5. ITSR values of mixtures with and without Advera

Favourable behaviour of mixtures without Advera, using only boron minerals with respect to moisture susceptibility, has also been investigated in the literature. Hydrophobic (water repellent) properties of boron minerals have been emphasized [35]. In this study, it was concluded that various modified materials, solvents, and their compatibility with each other, were effective on product yield and hydrophobicity. This specification of boron minerals has given valuable results showing that the conditioned samples do not contain the water completely in their structure, and thus the strength is not adversely affected.

### 4.4. Indirect tensile strength modulus (ITSM) test results

The ITSM values of WMA mixtures containing Advera and ulexite minerals decrease significantly with an increase in temperature. The ITSM values variation with the change in temperature is shown in Figure 6.

According to Table 6, as the temperature increases from 0 °C to 10 °C, the ITSM value decreases only by 44.40 % and 46.61 % for WMA added and raw reference samples, respectively. Again, the change for 5 % U-25 μ, 10 % U-25 μ and 5 % U+53 μ mixtures amounted to 47.56 %, 49.21 %, and 44.13 %, respectively, for an increase of 10 °C. The stiffness modulus at 0 °C of the 5 % U+53 μ asphalt mixtures was by 1.35 times higher than that of reference asphalt mixtures with WMA addition.

Table 5 ITS and calculated ITR values of all mixtures

Mixture type	Indirect tensile stress values [kPa]		ITSR values [%]
	Unconditioned	Conditioned	
Reference bitumen	1290.3	1097.1	85.03
B + 5 % Advera reference	1205.8	758.3	62.89
B + 5 % Advera + 5 % U-25 $\mu$	1042	587.1	56.34
B + 5 % Advera + 10 % U-25 $\mu$	1107.5	439.5	39.68
B + 5 % Advera + 5 % U+53 $\mu$	1215	599.4	49.33
B + 5 % Advera + 10 % U+53 $\mu$	1010.3	458.8	45.41
B + 5 % U-25 $\mu$	937.4	908	96.86
B + 10 % U-25 $\mu$	748.3	703.7	94.04
B + 5 % U+53 $\mu$	877.9	846.2	96.39
B + 10 % U+53 $\mu$	780.1	703.2	90.14

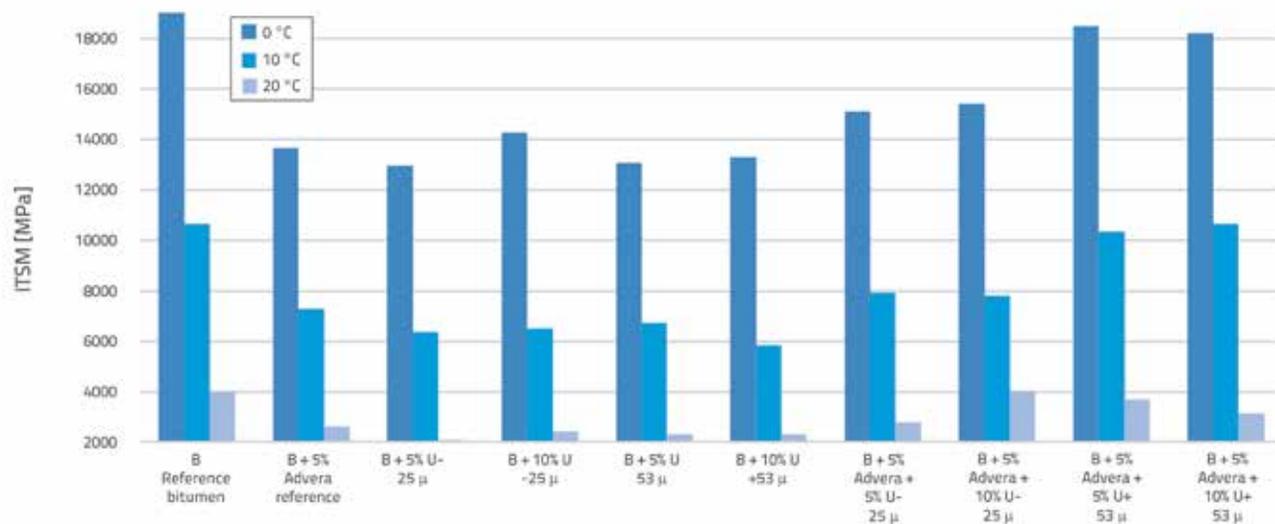


Figure 6. ITSM values of mixtures containing Advera and ulexite minerals

Table 6. Variation of ITSM values with Advera and ulexite minerals with temperature change

Mixture type	0 °C	10 °C	20 °C
Reference bitumen	19138	10640	4004
B + 5 % Advera reference	13646	7286	2597
B + 5 % Advera + 5 % U-25 $\mu$	15085	7910	2765
B + 5 % Advera + 10 % U-25 $\mu$	15400	7821	4042
B + 5 % Advera + 5 % U+53 $\mu$	18488	10328	3696
B + 5 % Advera + 10 % U+53 $\mu$	18195	10654	3128

A decrease in the stiffness modulus was observed in the WMA added reference sample. Since warm mix asphalt cannot be obtained without the use of additives, it is also necessary to use additives. Here, this adverse situation with the use of additives has been overcome by the addition of WMA additive + boron minerals. Namely, the stiffness modulus value of mixtures containing ulexite at both 5 % and 10 % of + 53  $\mu$

sizes improved by 1.35 times for 0 °C, 1.43 times for 10 °C, and 1.31 times for 20 °C, respectively, compared to reference asphalt mixtures with WMA. Already with the use of nano sized boron minerals, warm mix asphalt admixtures were able to avoid adverse effects such as the lack of adhesion and loss of strength. It is evident from these results that this substance has confirmed its usefulness. Reference bitumen was slightly

improved with the addition of only 5 % U-25  $\mu$  and 10 % U-25  $\mu$ ; greater improvement was observed with 5 % U+53  $\mu$  and 10 % U+53  $\mu$  additions when only WMA was added.

As a result, ITSM values regarding reference bitumen and Advera reference indicated that the utilization of WMA additive increases the stiffness of mixtures; Regarding Advera reference and Advera + ulexite additive mixtures, ITSM values indicated that the usage of boron minerals increases the stiffness value compared to Advera reference mixtures.

## 5. Conclusions

Low Temperature (Bending *Beam* Rheometer-*BBR*), Marshall Stability, Indirect Tensile Strength Modulus and Susceptibility tests were conducted in this study, in which nano sized ulexite minerals were added to the warm mix asphalt. This study researching the effect of ulexite mineral in warm mix asphalt at nano-scale is the first study that has been presented in literature about this particular issue. The following results were obtained:

- It can be said that, besides the dimension of ulexite additive, its quantity is also important. Thus 5 % of additives gave better results than 10 %, and the same situation was observed in the case of formation of voids.
- The nano ulexite additive shows resistance by reducing the tendency of cracking at low temperatures of WMA.
- Although the highest VFA and lowest VMA values were obtained at B + 5 % Advera + 5 % U+53  $\mu$  mineral additive, the highest air voids (Va) values were obtained at B + 5 % Advera + 10 % U+53  $\mu$  additive.
- A higher air voids value in mixtures containing B + 5 % Advera + 10 % U+53  $\mu$  dimensional minerals can be explained by the fact that submicron sized materials form a highly specific area.

- While the bitumen reference sample gives a negative result compared to the Advera reference, Advera + ulexite contribution gives a positive result.
- Both the stability and flow are higher in the sample obtained with the mixture of B + 5 % Advera + 5 % U-25  $\mu$  compared to other samples. The Marshall ratio value, which is the ratio of stability to flow has been preserved, just like in other mixtures. VMA and VFA values are seen to be slightly below the standards. This seems to be a negative situation. But, in this case, two positive results were noted. One of them is that the WMA mixing temperature, which is 135 °C, can be further reduced, that is, it can be reduced to 120 °C, and the other is an improvement in workability.
- Nano boron minerals have been preferred for WMA to overcome the problems such as the lack of adhesion and loss of strength caused by the use of warm mix asphalt. It is also apparent from these results that the suitability for use has been confirmed.
- ITS values are generally reduced in mixtures made with boron minerals, The result is that the loss of strength due to conditioning is not significant. The loss of strength with conditioning is about 3-4 % for ulexite added samples. This is why such asphalt pavements can be preferred in continually rainy climates such as in the Black Sea region.
- ITSR results with WMA Advera additive were found to be well below the acceptable limit.
- The results of ITSM experiments performed at 0 °C, 10 °C and 20 °C point to the highest hardness value.
- At 20 °C, it was reached with 5 % U+53  $\mu$  mixture and, at 10 °C, it was reached with 10 % U+53  $\mu$  mixture. In the case of experiments with only nano boron and only Advera additive, there was a slight decrease in dynamic load compared to the raw bitumen. Although it was a negative effect compared to the raw bitumen reference, the combination of the two led to general improvements. This shows that both must be used to obtain WMA.

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