



## EFFECT OF ZEOLITE ADDITION TO MODIFIED BITUMEN FOR APPLICATION IN WEARING COURSE

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### Abstract

Generally, asphalt mixtures intended for wearing surfaces subject to heavy traffic are made on the basis of polymer-modified binders. Their production requires high energy consumption. Warm mix asphalt (WMA) technologies are an excellent solution for fulfilling these requirements. Foaming based WMA have shown great potential in reducing the mixing and compaction temperature of asphalt mixtures by decreasing the viscosity of the binder. Foaming based WMA can be obtained by adding to the binder water-bearing additives such as zeolites. This paper presents the results of a study of two zeolite additives differing in their crystal structure for polymer modified bitumen binder (PMB 45/80-55): one is natural zeolite of the clinoptilolite type, and the other is synthetic zeolite Na-P1 produced from fly ash. Both additives, previously soaked with water, were added in amounts of 5% by weight of the modified binder. Based on the results, obtained from the conducted tests (i.e. softening point, penetration, dynamic viscosity and cohesion), it was concluded that both zeolites do not significantly affect the viscoelastic properties of PMB 45/80-55. Only the effect on cohesion was observed, indicating that the binder becomes stiffer, making the pavement less resistant to cracking. It was determined that from the perspective of the impact on the viscoelastic properties of the modified binder PMB 45/80-55, the best solution is to use a natural zeolite of the clinoptilolite type. The test results obtained on modified bitumen with the addition of zeolites were compared to the results of modified binders with styrene-butadiene-styrene copolymer (SBS) and crumb rubber (CR). It was found that modified binders with SBS and CR shows comparable properties to zeolite-modified bitumen.

*Keywords: warm mix asphalt, natural zeolite, synthetic zeolite, modified bitumen*

### 1 Introduction

One of the key issues in road pavement design is the optimal selection of materials for the pavement structure layers. The wearing course is the first layer, exposed to direct traffic. Its purpose is to protect the lower layers from mechanical and environmental influences to ensure safe driving and a high level of travel comfort. For pavements with heavy and very heavy traffic, more restrictive requirements for resistance to permanent deformation, fatigue and low-temperature cracking must additionally be met. It was established that the properties of the selected binder are closely correlated with the resistance to deformation and durability of the pavement structure [1]. In order to improve the viscoelastic properties of bitumen in recent decades use of various types of modifiers i.e.: anti-stripping agents, crumb rubber, polymers, natural asphalts [2]. However, the production of hot mix asphalt (HMA) mixtures using such modified binders requires high energy consumption and leads to the emission

of a huge amount of greenhouse gases. Due to policies related to environmental strategy in the US, more than 30% of all mixtures are already produced in WMA technology. In European countries, i.e. France and Sweden, the overall percentage of WMA technology is more than 10% [3].

WMA technology, compared to HMA technology, has the major advantages: extends the construction season in spring and autumn, reduces energy consumption by 25-30%, improves comfort and safety at work, improves workability of the mixture, reduces air pollution by about 20% [4, 5]. It was found that reducing the temperature of the production of asphalt mixture by 10 °C, contributes to saving 1 liter of fuel and decreasing CO<sub>2</sub> emissions by 1 kg per 1 ton of finished product [6]. A number of products are available on the market to reduce the production temperature of conventional asphalt mixtures by about 20-60 °C [3]. There are three main categories of WMA production: chemical additives, organic additives and foaming technology [7]. Foaming technology is the oldest and most popular technology for reducing the temperature of asphalt mixture production, which is divided into two technologies: water-based and water-containing [8]. Water-based technology involves the direct addition of pressurized water at a temperature of around 25 °C to heated bitumen (160-180 °C). Water is evaporated during the mixing process, which contributes to the generation of foam with a high specific surface area, which increases the volume of the bitumen and reduces its viscosity [9, 10]. An alternative way to foaming bitumen is water-containing technology. It involves adding zeolites (water-bearing additives) to the bitumen, which contain a certain amount of water in their honeycomb micro-structure, known as “zeolite water” [11]. During interaction with the hot bitumen binder, the water stored in the crystalline structure is gradually released (over about 2-3 hours), leading to the generation of micro-foam. This process decreases the viscosity of bitumen, thereby increasing its ability to coating the aggregate surface and improving the workability of the finished mixture [12].

By origin, natural and synthetic zeolites are distinguished. The group of natural zeolites includes about 100 hydrated crystalline aluminosilicate minerals. For economic reasons, minerals found in the form of deposits were recommended for bitumen foaming: clinoptilolite, phillipsite, chabazite and mordenite. Synthetic zeolites, consisting of alkali metal aluminosilicates, are artificially formed from mineral materials (clay minerals and silica group minerals), chemical reagents and by-products of coal combustion in power plants [8]. Zeolites used in WMA technology must meet specific criteria. One of the most important is the lack of negative impact on the viscoelastic properties of base bitumen which will be modified.

The objective of this study is to evaluate the possibility of using two types of zeolites, which differ in their crystalline structure, to modify PMB 45/80-55 binder for application in wearing course. One of the additives is a natural zeolite of the clinoptilolite type, the other is a synthetic zeolite Na-P1, obtained from fly ash. The possibility of using zeolites was determined by evaluating the effects on the viscoelastic properties of PMB 45/80-55 binder. The results of zeolite-modified bitumen were also compared with the results of bitumen modified with SBS copolymer and CR.

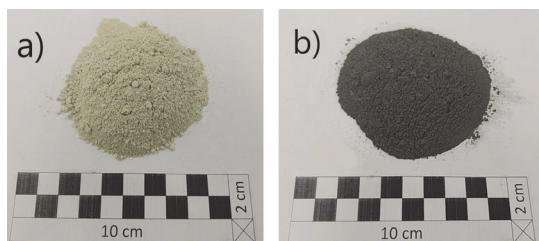
## 2 Materials and methods

### 2.1 Polymer modified bitumen

In this study conventionally SBS modified binder ORBITON 45/80-55 was used. It is one of the most widely used modified bitumen in Poland for application in all types of asphalt mixtures in wearing course. Used PMB 45/80-55 is manufactured in accordance with EN 14023 specifications. According to European requirements, PMB bitumen producers are not required to provide the percentage of polymer used for modification.

## 2.2 Warm mix additives

Two zeolite additives produced at Lublin University of Technology to the modified bitumen binder were used: one is natural zeolite of the clinoptilolite type, and the other is synthetic zeolite Na-P1 (Fig. 1). Natural zeolite clinoptilolite (ZN-C) in a form of zeolitic tuff was acquired from Sokyrnytsya deposit (Transcarpathian region, Ukraine). In contrast, synthetic zeolite Na-P1 was produced at the Lublin University of Technology (Poland).



**Figure 1** Pictorial presentation of the additives used in this study: (a) clinoptilolite, (b) Na-P1

The selected natural clinoptilolite, in a powder form with a white to yellowish color, contains more than 70% pure clinoptilolite in its composition. The rest of the composition consists of cristobalite, quartz, feldspar and clay minerals. The structure of clinoptilolite is made up of two-dimensional channels formed by eight-membered rings measuring  $4.1 \times 4.1 \text{ \AA}$  and ten-membered rings measuring  $2.8 \times 4.8 \text{ \AA}$ . The maximum dimensions of the grains formed by clinoptilolite are about  $10 \text{ \mu m}$  long,  $15 \text{ \mu m}$  wide and  $0.2 \text{ \mu m}$  thick [13]. Natural zeolite also has a number of specific properties, the most important of which include high thermal stability and resistance to aggressive agents, reversible hydration and dehydration [14].

Synthetic zeolite Na-P1 with a 70% purity was obtained through a hydrothermal reaction by converting fly ash (derived from coal combustion) and an aqueous solution of NaOH. The structure of Na-P1 is made of two four-membered rings forming an eight-membered channel with dimensions of  $3.1 \times 4.5 \text{ \AA}$  and  $2.8 \times 4.8 \text{ \AA}$ . The dimensions of the synthetic zeolite grains are  $1 \text{ \mu m}$  in length,  $0.2 \text{ \mu m}$  in width and  $0.1 \text{ \mu m}$  in thickness [13].

## 2.3 Sample preparation

In this study, the zeolite-modified binder was prepared based on the experiences presented in the papers [8, 13, 15]. “Zeolite water”, accumulated in the crystal structure, is released in the temperature range from  $100$  to  $400 \text{ }^\circ\text{C}$ . Higher temperatures cause a greater release of water, which affects the quantity and quality of the microfoam formed. As the temperature at which the binder was modified with zeolites was  $175 \text{ }^\circ\text{C}$ , the zeolite materials were pre-saturated. Clinoptilolite was mixed with water at a ratio of 1:3 to dry weight, while Na-P1 was mixed at a ratio of 3:1.

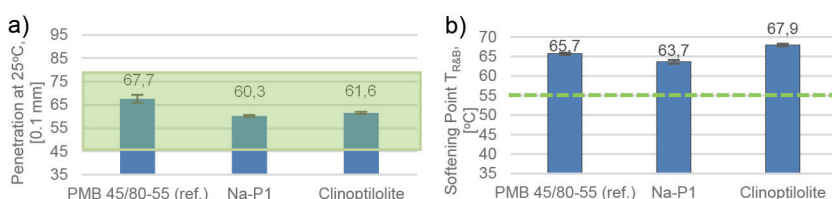
The amount of water was selected in a way that would not cause problems with the enveloping of aggregate surfaces. The process of sample preparation was as follows: zeolite was added to the preheated binder at a rate of 5% (by weight of the binder). The components were mixed by hand for 1 minute until foam was formed. The sample was placed again in a drying oven for 30 minutes for stabilization, after which the viscoelastic properties of the obtained modified binders were determined.

## 2.4 Testing methods

All binders used in this study were tested with conventional classification tests such as penetration at 25°C according to EN 1426, softening point (“Ring and Ball” method) according to EN 1427, dynamic viscosity according to EN 13302, elastic recovery according to EN 13398 and force ductility (cohesion) in accordance with EN 13589. Visco-elastic properties of modified bitumens were obtained for non-aged binders. Based on the test results of penetration and softening point, the penetration index (EN 12591) was calculated, which indicates the thermal sensitivity of binder.

## 3 Results and analysis

The consistency of zeolite-modified binders was evaluated based on the results obtained in a penetration test at 25 °C (Fig. 2a). The green area in Figure 2a indicates the penetration range within which PMB 45/80-55 should fall, according to EN 14023. It should be concluded that zeolite additives have a stiffening effect on the reference binder. It was observed a decrease in penetration by 11% with Na-P1 synthetic zeolite and by 9% with clinoptilolite in relation to the reference binder. The obtained results (Fig. 2a) are compatible with previous studies reporting a decrease in binder penetration after the addition of zeolites [13, 14]. The stiffening effect is a natural phenomenon caused by the presence of solids (in form of dust) in the less rigid bitumen matrix. The stiffening is also influenced by the interfacial effect occurring between zeolite particles and binder.

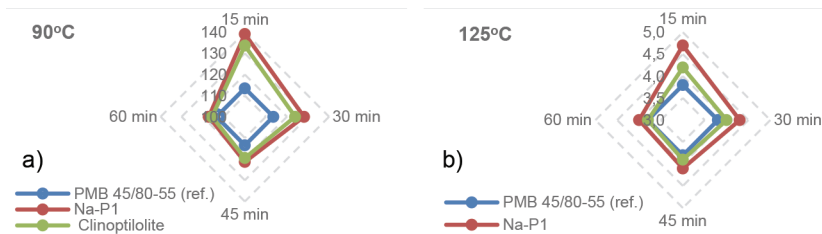


**Figure 2** The results of a) penetration and b) softening point tests for the PMB 45/80-55 bitumen with the addition of Na-P1 and clinoptilolite zeolites

Figure 2b shows the effect of zeolite addition on the softening point of PMB 45/80-55. The idea of this test is to determine the conventional temperature at which bitumen binder changes from a viscoelastic to a viscous state. According to EN 14023, the softening point of PMB 45/80-55 should be above 55 °C. Modification of reference binder with water-soaked zeolites shows no significant effect on change in softening point. After adding Na-P1 synthetic zeolite to binder, a 2.0 °C decrease in softening point was observed. The most favorable changes, in terms of rutting resistance were observed using clinoptilolite (softening point increase by 2.2 °C in comparison with the reference binder).

Based on the results of penetration and softening point tests, the penetration index  $PI$  was estimated, a lower value of which indicates greater thermal sensitivity of tested binder. For PMB 45/80-55, the  $PI$  value was 2.92. With the addition of Na-P1 synthetic zeolite, the thermal sensitivity of binder increases, as evidenced by a lower penetration index value ( $PI = 2.25$ ). The most favorable properties, in terms of temperature resistance, were obtained by binder modified with clinoptilolite ( $PI = 3.07$ ).

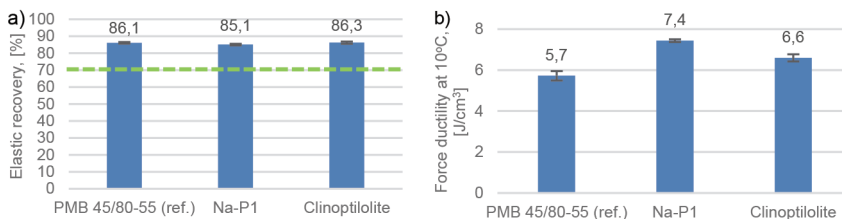
The viscosity is an important parameter to determine the possibility of proper enveloping of the aggregate with a thin film of bitumen. In this study, viscosity changes were evaluated using a Brookfield’s viscometer. Viscosity was determined at 90 °C and 125 °C at intervals of 15, 30, 45 and 60 minutes, counting the time from placing the sample in the viscometer (Fig. 3).



**Figure 3** The results of dynamic viscosity (Pa·s) for the PMB 45/80-55 bitumen with the addition of Na-P1 and clinoptilolite zeolites measured at: a) 90°C, b) 125 °C (used different scales for better legibility)

The effect of decreasing dynamic viscosity over time was observed in each of the zeolite-modified binders. This phenomenon occurs due to the gradual release of “zeolite water” that has been incorporated into the crystalline structure of the modifier. The most significant changes in viscosity were recorded in the time interval of 15-30 min for Na-P1 zeolite-modified binder: at 90 °C there was a decrease of 8.0%, at 125 °C - by 8.5% in relation to PMB 45/80-55. The rise of temperature causes faster “zeolite water” release, as evidenced by the greater change in viscosity over time at 125 °C. After 45 min of testing, the viscosity of zeolite-modified binders stabilizes. Similar results were also reported in the papers [8, 16]. The six-fold higher mesopore volume of the Na-P1 synthetic zeolite, which has a better ability to absorb binder particles, determines its higher viscosity compared to clinoptilolite [13]. By introducing insoluble solids such as zeolites into the binder, there was a slight increase in viscosity within 3-5% in comparison with PMB 45/80-55.

Evaluation of elastic recovery of binders makes it possible to indirectly estimate the resistance of mixtures using this binder to rutting. According to EN 14023, the value of elastic recovery at 25 °C should be above 70% (Fig. 4a). The results show no negative impact on this parameter. In the modification process, there is a phenomenon of “wrapping” of solids (zeolites) through the SBS copolymer network formed in PMB 45/80-50. A non-significant 1% decrease in elastic recovery was observed for Na-P1 zeolite-modified binder, while the recovery values for clinoptilolite are comparable to reference binder.



**Figure 4** The results of a) elastic recovery and b) force ductility for PMB 45/80-55 bitumen with the addition of Na-P1 and clinoptilolite zeolites

Fig. 4b shows the results of cohesion of PMB 45/80-55 binder foamed by adding Na-P1 and clinoptilolite zeolites. It is assumed that higher cohesion between binder molecules, indicates a more consolidated material structure. Therefore, it can be predicted that asphalt mixtures using high adhesion bitumen will have higher fatigue life. According to EN 13589, cohesion should be determined in a ductilometer at 5 °C. Because specimens with zeolite-modified binder were damaged at this temperature, the temperature was raised to 10 °C. The obtained results of zeolite-modified binders are compared with those of binders modified with 5% of SBS copolymer and 20% of crumb rubber. According to the results reported in the paper [17], most of the viscoelastic properties of bitumen with the addition of SBS and crumb rubber are comparable to the properties of PMB 45/80-55 binder modified with zeolite.

However, the viscosity values at 90 °C for bitumen modified with 5% of SBS are 227.1 Pa·s, and 996.3 Pa·s for bitumen modified with 20% of crumb rubber. This is an increase of 95% and 750%, respectively, compared to the viscosity of zeolite-modified binders. All of this shows the necessity of raising the technological temperatures during the production, transport and laying of mixtures with SBS and crumb rubber binders. Therefore, from an economical, technological and environmental point of view, a better way is to modify bitumen with zeolites.

## 4 Conclusions

Conducted analysis of test results showed that modifying additives such as synthetic zeolite Na-P1 and clinoptilolite in the amount of 5% (in relation to the weight of the binder) do not significantly affect the viscoelastic properties of PMB 45/80-55 and mostly meet all European requirements. Only an effect on binder cohesion was observed, indicating a negative increase of binder stiffness. After analyzing the above results, it was concluded that modification of PMB 45/80-55 binder with clinoptilolite at 5% is a better solution, compared to Na-P1 synthetic zeolite. To verify the preliminary results of modified binders, further studies of the technical properties of asphalt mixtures are needed.

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