PAPER • **OPEN ACCESS**

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To cite this article: Judita Gražulyt *et al* 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1202** 012017

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OPTIMISATION OF NANO-ZnO AND NANO-SiO$_2$ MIXING TIME FOR BITUMEN MODIFICATION

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Abstract. Nanotechnologies have gradually penetrated to the field of bitumen modification especially where durable asphalt mixtures have to be designed. Longer mixing time, higher temperatures or/and higher rotation (shearing) speeds are needed to increase the dispersion of nanoparticles in bitumen. However, this is not necessarily beneficial to the physical and mechanical properties of the final material. As a result, in this study nano-zinc oxide (nano-ZnO) and nano-silica (nano-SiO$_2$) mixing time for bitumen modification was optimized considering the physical and mechanical properties of the final bitumen. For this purpose bitumen PMB 25/55-60 was modified with nanoparticles at 180 °C using a laboratory high-shear mixer at a rotation speed of 4000 rpm for different modification time selected on the basis of literature review (60 and 90 minutes). Penetration, softening point, viscosity at 135 °C, recovery and non-recoverable creep compliance (multiple stress creep and recovery test) at 60 °C were measured in order to determine the optimal mixing time. The results showed that 60 minutes ensures the dispersion of nano-ZnO and nano-SiO2 in the bitumen PMB 25/55-60 and longer mixing time do not have a significant effect on the properties of nano-ZnO and nano-SiO2 modified bitumen (the difference was less than 7%).

Keywords: bitumen, nano-zinc oxide (nano-ZnO), nano-silica (nano-SiO2), modification time, nanoparticles

Introduction

Bitumen in asphalt pavements is constantly affected by traffic and climate, which inevitably degrades its physical, mechanical and chemical properties. This process is called aging. In recent decades, the problem of bitumen aging has received special attention. To improve the resistance of bitumen to aging, antioxidant additives are incorporated into bitumen. However, they are organic substances and their properties gradually change. It limits their use in the long-term (Du et al., 2015).

Nowadays, nanotechnology is playing an important role in modifying materials to ensure the high quality. Nano particles are defined as a particles with at least one dimension that is less than 100 nm (Yang et al., 2013). Nanomaterials such as nano-zinc oxide, nano-silica, nano-titanium dioxide, nano-clay and carbon nanotubes are suitable for bitumen modification. The conducted studies show that nanomaterials strengthen the binding properties of bitumen, increase the durability of the bitumen and resistance to transport loads. For example, asphalt pavement become more resistance to aging and increases resistance to rutting (Ezzat et al., 2016). Also, nanomaterials give bitumen greater ductility, increase softening temperature and reduce penetration (Rezaei et al., 2016, Ziari et al., 2014). As a result, nanoparticle-modified bitumen becomes more resistant to temperature cracks, permanent deformation and fatigue (Alhamali et al., 2016, Yusoff et al., 2019).

One of the most commonly used nanomaterials in bitumen modification is nano-zinc oxide (nano-ZnO) and nano-silica (nano-SiO$_2$). Nano-ZnO is an organic compound that looks like a milky white powder and is insoluble in water. Previous studies indicated that bitumen modified with nano-ZnO has lower stiffness, higher softening temperature, ductility, viscosity, resistance to rutting, aging and resistant to temperature cracks (Du et al., 2015, Zhang et al., 2018)

Nano–SiO$_2$ is an inorganic dioxide that looks like a white powder and is also insoluble in water. Nano-SiO$_2$ added in bitumen improves pavement performance. For example, pavement becomes more resistant to temperature cracks rutting, aging and fatigue (Alhamali et al., 2016, (Yusoff et al., 2019, Lazzara et al., 2010, Lee et al., 2013).

In order to ensure appropriate dispersion of nanoparticles to bitumen, mixing has to be performed using special equipment and specific mixing time, temperature and rotation (shearing) speed. However, different modification conditions are used among different scientist and there is no universally accepted technique. For example, Khairul et al. (2018) slowly added nano–ZnO in bitumen 60/70 and mixed them with high shear mixer at a rotation speed of 2000 rpm for 30 min at 135–150 ºC. While other scientists, the rotation speed and mixing time reduced up to 12000 rpm and 4–5 min, respectively (Azarhoosh et al., 2018). Also, bitumen modification with nano-ZnO particles was conducted at a

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rotation speed of 2000–5000 rpm for longer period, i.e. 60–90 min (Du et al. 2015, Zhang et al. 2015, Liu et al. 2015). In previous researches, bitumen was also modified with nano–SiO_2. Sezavar et al. (2019) done it with with high shear mixer at 4000 rpm and mixed for 30 min at 163 ºC. Other scientists, for modification also used a high shear mixer, but the rotation speed was lower (1500–3000 rpm) and mixing time was longer (for 60 min). The temperature was kept at 145–160 ºC (Alhamali et al., 2016, Ezzat et al., 2016, Yusoff et al., 2019). Saltan et al. (2017) nano–SiO2 added at 160 ºC and mixed at a rotation speed of 4000 rpm for 120 min.

It is obvious that modification conditions as time, temperature and rotation speed are still not optimized although it has a significant effect. For example, mixing the nanomaterial for too short or at too low temperature does not ensure the dispersion of the nanomaterial, on the other hand, mixing too long or at too high temperature, the bitumen will age and this will affect its performance. Therefore, the purpose of this work is to evaluate the effect of mixing time on the physical and mechanical properties of nano–ZnO and nano–SiO_2 modified bitumen.

1. Experimental research

In this study, polymer modified bitumen PMB 25/55-60 was modified with nanomaterials. Chemical composition and physical properties of bitumen PMB 25/55-60 are shown in Figure 1 and Table 1. The bitumen was modified with 6% nano-ZnO or 1% nano-SiO_2. Table 2 represents the physical and chemical properties of nano-ZnO and nano-SiO_2.
The bitumen heating temperature for bitumen modification was selected in accordance with the requirements of standard EN 12594. Bitumen PMB 25/55-60 was heated at 180 ºC in oven until it flowed fully. A laboratory high-shear mixer with rotation speed of 4000 rpm was used to disperse nano–ZnO or nano-SiO_2 into bitumen. Two different mixing times (60 and 90 minutes) were selected based on the literature review. To acquire a homogeneous dispersion, nanoparticles were gradually added into the bitumen.

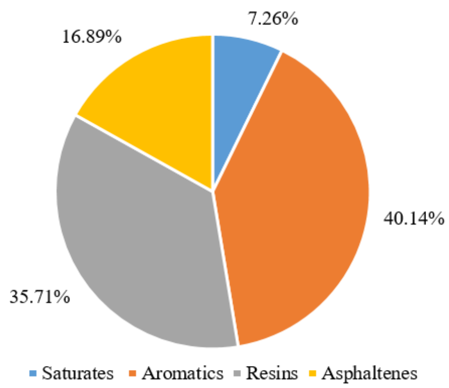

Figure 1. Chemical composition of bitumen PMB 25/55-60

Table 1. Physical properties of bitumen PMB 25/55-60

Characteristic	Test standard	Value
Softening Point (°C)	EN 1427:2015	65.0
Penetration at 25 °C (dmm)	EN 1426:2015	31.2
Viscosity at 135 °C (mPa*s)	EN 13302:2018	2767.7
Elastic Recovery (%)	EN 13398:2018	72.8

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Table 2. Properties of nano-ZnO and nano-SiO_2

Properties	Nanomaterials	
	nano-ZnO	nano–SiO_2
Particle size (nm)	30	15
Purity (%)	99.5	99.5
Density at 20 °C (g/cm^3)	5.606	-
Melting point (°C)	1975	>1700
Physical appearance	milky white powder	white powder

The effect of mixing time on the physical and mechanical properties of nano–ZnO and nano–SiO_2 modified bitumen were determined by penetration, softening point, dynamic viscosity, recovery and non-recoverable creep compliance. The penetration was determined according to European standard EN 1426:2015. The softening point was measured according to EN 1427:2015 by using a ring and ball apparatus. Brookfield viscometer was employed to measure the dynamic viscosity at 135 °C according to standard EN 13302:2018.

Mechanical properties of the modified bitumen were determined using Anton Paar M302 dynamic shear rheometer (DSR). Multiple Stress Creep and Recovery (MSCR) test was performed according to AASHTO TP 70:2013 and EN 16659:2016. Tests were conducted at 60 °C temperature and stress of 0.1 kPa and 3.2 kPa. Therefore, a 1 mm gap and 25 mm diameter plates were used.

2. Results and analysis

The effect of mixing time on the basic properties of nano–ZnO (6%) and nano–SiO_2 (1%) modified bitumen PMB 25/55-60 are shown in Figure 2–4. It was observed from Figure 2 that both mixing time and nanomaterial type only slightly affect the penetration. It varied from 30.5 dmm (1% nano-SiO_2 and mixing time – 90 minutes) to 32.3 dmm (1% nano-SiO_2 and mixing time – 60 minutes) while reference value was 31.2 dmm. The softening point of the nanomaterial modified bitumen increased compared to the reference bitumen from 65.0 °C to 67.6–69.0 °C. However, the effect of longer mixing time on softening point was different depending on the nanomaterial type: it decreased from 68.5 °C to 67.6 °C for nano-ZnO while for nano-SiO_2 – increased from 67.7 °C to 69.0 °C (Figure 3). As shown in Figure 4, the viscosity of nanomaterial modified bitumen increased by 5–8% irrespective of mixing time, except for nano-ZnO modified bitumen that was mixed for 90 minutes. For this one, it decreased by 2.2%. As nano–SiO_2 was added into bitumen PMB 25/55-60 and mixing time was prolonged from 60 minutes to 90 minutes, viscosity increased from 2977 mPa·s to 3008 mPa·s.

The MSCR test results are shown in Figure 5–6. It is obvious that the use of nanomaterials to modify bitumen PMB 25/55-60 leads to higher recovery and lower non-recoverable creep compliance irrespective of both stress level and nanomaterial type. At stress level of 0.1 kPa, recovery increased from 49% to 57–58% and 59–60% while non-recoverable creep compliance decreased from 0.19 1/kPa to 0.13–0.14 1/kPa and 0.12–0.13 1/kPa respectively for nano–ZnO and nano–SiO_2 modified bitumen. The increase in stress level from 0.1 kPa to 3.2 kPa resulted in the same trend: recovery increased from 37% to 44–46% and 46–48% while non-recoverable creep compliance decreased from 0.24 1/kPa to 0.18–0.20 1/kPa and 0.17–0.18 1/kPa respectively for nano–ZnO and nano–SiO_2 modified bitumen. As observed from Figures 5–6, prolonged mixing time slightly affected test results. In all cases, recovery slightly increased and non-recoverable creep compliance decreased.

In order to better evaluate the impact of nanomaterials (nano–ZnO and nano–SiO_2) and mixing time on the physical and mechanical properties of bitumen PMB 25/55-60, the change of each property in percentage was calculated (Table 3–4). The results show that nanomaterials have significantly higher effect on the mechanical properties of PMB 25/55-60 comparing to the physical properties. The change in penetration, softening point and viscosity was lower than 9% while recovery and non-recoverable creep compliance increased (decreased) by 15–35% depending on both nanomaterial type and mixing time. Focusing only on the effect of mixing time, it was observed that change in each property is lower than 6% and 7% for nano–ZnO and nano–SiO_2, respectively. This kind of change in bitumen properties is not significant and keeping in mind that longer mixing time may accelerate aging process in the bitumen, which is undesirable, mixing time of 60 minutes for bitumen modification with nanomaterials is assumed as optimal. As a result, slow addition of nanomaterials into bitumen at 180 °C and mixing with a high-speed mixer for 60 minutes at a speed of 4000 rpm is considered as the most rational technology to modify bitumen with nanomaterials. This technique ensures the homogenous dispersion of nanomaterials.

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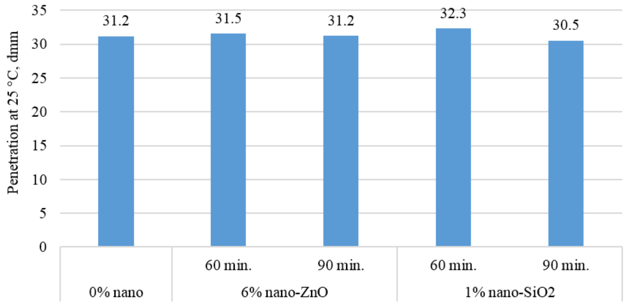

Figure 2. Penetration at 25 °C

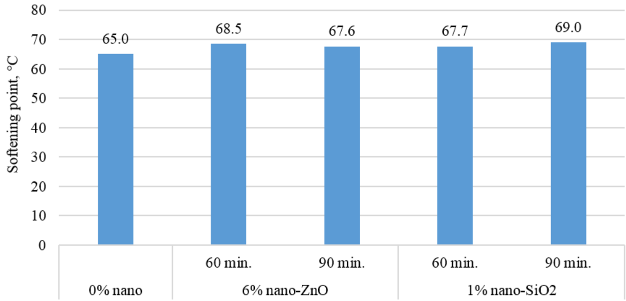

Figure 3. Softening point

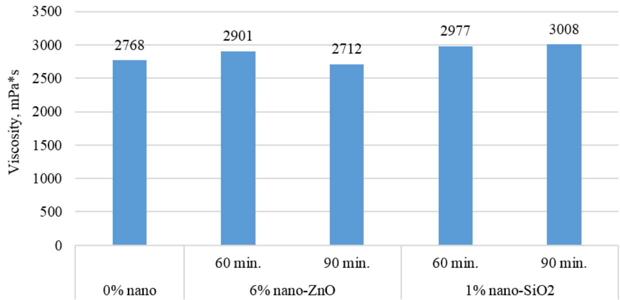

Figure 4. Dynamic viscosity

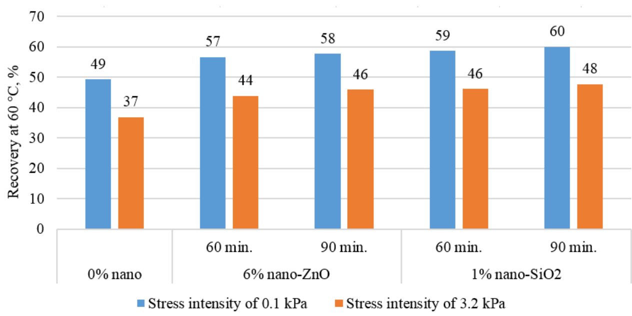

Figure 5. Recovery at 60 °C

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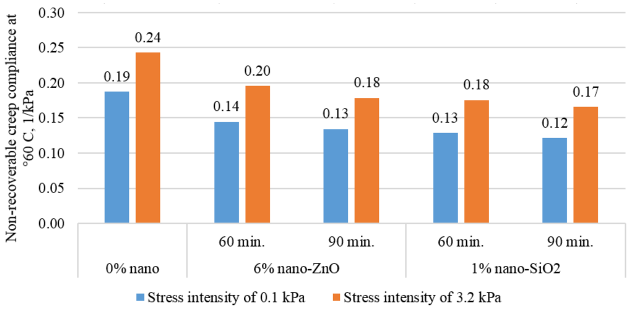

Figure 6. Non-recoverable creep compliance at 60 °C

Table 3. Effect of nano-ZnO and prolonged mixing time on bitumen performance

Change in property	6% nano-ZnO		Influence of longer mixing time
	60 min.	90 min.	
Penetration at 25 °C (%)	+1.1	+0.1	1.0
Softening point (%)	+5.4	+3.9	1.5
Viscosity at 135 °C (%)	+4.8	-2.0	6.8
Recovery at 0.1 kPa and 60 °C (%)	+15.2	+17.3	2.1
Recovery at 3.2 kPa and 60 °C (%)	+19.1	+24.6	5.5
Non-recoverable creep compliance at 0.1 kPa and 60 °C (%)	-22.7	-28.3	5.6
Non-recoverable creep compliance at 3.2 kPa and 60 °C (%)	-19.4	-26.4	7.0

Table 4. Effect of nano-SiO_2 and prolonged mixing time on bitumen performance

Change in property	1% nano-SiO_2		Influence of longer mixing time
	60 min.	90 min.	
Penetration at 25 °C (%)	+3.5	-2.2	5.8
Softening point (%)	+4.1	+6.1	2.0
Viscosity at 135 °C (%)	+7.6	+8.7	1.1
Recovery at 0.1 kPa and 60 °C (%)	+19.3	+21.8	2.5
Recovery at 3.2 kPa and 60 °C (%)	+25.2	+29.5	4.2
Non-recoverable creep compliance at 0.1 kPa and 60 °C (%)	-31.2	-35.2	4.0
Non-recoverable creep compliance at 3.2 kPa and 60 °C (%)	-27.6	-31.8	4.2

Conclusions

1. The conducted study showed that longer mixing time (90 minutes) only slightly (6–7%) changes bitumen characteristics (penetration, softening point, viscosity and resistance to permanent deformation) comparing to mixing time of 60 minutes.

2. The slow addition of nanomaterials to bitumen at 180 °C temperature and mixing with a high-speed mixer for 60 minutes at a speed of 4000 rpm is considered as the most rational technology to modify bitumen with nanomaterials. It leads to the homogenous dispersion of nanomaterials and prevents bitumen from premature aging that might happen because of too long mixing at such high temperature.

3. Laboratory tests with bitumen PMB 25/55-60 modified with either 6% nano-ZnO or 1% nano-SiO_2 showed that nanomaterials harden the bitumen and as a result, lead to higher softening point, viscosity and resistance to permanent deformation. In fact, the effect of nanomaterials on bitumen mechanical performance is significantly higher than on physical properties.

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4. Since this study was limited in terms of test methods and only one amount of each nanomaterial was tested, further comprehensive studies need to be carried out in order to get a full picture of effect of nanomaterial on bitumen performance especially on mechanical properties and identify the optimal content of nano-ZnO and nano-SiO_2 for bitumen modification. Moreover, a special attention has to be paid on resistance to low temperature cracking because as this study has shown nanomaterials harden the bitumen and it is the main cause for this type of cracking.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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