IOP Conf. Series: Materials Science and Engineering **236** (2017) 012007 doi:10.1088/1757-899X/236/1/012007

The influence of nanoclay on the durability properties of asphalt mixtures for top and base layers

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Abstract. To avoid traffic congestion, due to road works, a continuous research into asphalt pavement and especially its durability is of great importance. This research focuses on improving the mechanical performance and the durability of asphalt mixtures by nanoclay modified bitumen. This promising technique of introducing nanoclays or nano particles into bitumen could offer an significant improvement on the fatigue properties and rutting performance and thus the durability of the asphalt top layer.

1. Introduction

For the heavely used “congested” Belgian road network, a continuous research into asphalt pavement and especially its durability is of great importance to avoid traffic congestion, due to road works.

This research focuses on improving the mechanical performance and the durability of asphalt mixtures by nanoclay modified bitumen.

A specific asphalt mixture type for base layers in Flanders, AC 14 base 35/50 (EN 13108-1), using a relatively hard bitumen was modified. Both physical and rheological properties of the modified binder were evaluated. This included the determination of the penetration and softening point and the characterization of dynamic rheological parameters, by using a Dynamic Shear Rheometer (DSR).

The prefix ‘nano’ indicates the occurrence of a material that measures less than 100 nm, in at least one dimension. From literature, general trends on organic montmorillonite nanoclay (OMMT) modified bitumen can be derived. It is indicated that the penetration decreases and the softening point increases by adding nanoclays[1, 2, 3, 4, 5, 6]. An explanation can be found by the reinforcement effect of the silicate layers on the bitumen [7]. Based on tests with a DSR, the bitumen seems to become more elastic and stiffer [2, 8, 9, 10, 11]. This effect is more pronounced at high temperatures and/or low frequencies. The viscosity increases also after the OMMT modification [2, 6, 8, 9, 12]. The indirect tensile strength does not change at 5°C and 25°C but does improve at 40°C [1, 2, 5, 12]. In addition, nanoclay can form a barrier in bitumen through which penetration of oxygen and water is prevented [2]. The effects of the modification by nanoclay are more pronounced by increasing the amount or when using soft bitumen. Nevertheless, there is still a need for sufficient research on the use of nano-modified bitumen in asphalt. Especially as there are almost no research publications regarding the application of nanoclay in harder bitumen, a type which is preferably used in Belgian mixtures to provide rutting, though cracking must be avoided. This exploratory study will evaluate physical and rheological properties of a harder bitumen modified with nanoclay. Additionally, the modified mixture was also processed into an asphalt mixture of which the changes in mechanical and physical properties were identified.

2. Experimental

Because adequate research on the use of nanoclay in hard bitumen is lacking, the relevance of the subject is tested in this study. The study is carried out on an base layer because the literature shows that nano-modified bitumen can have a positive influence on durability properties.

2.1. Materials

The bitumen B35/50 used in this study is an oil derivative from Dunkirk provided by Total. The binder has a softening point of 52,2°C and a penetration of 41.0 dmm. The binder is used in an AC base 35/50 mixture. The sandstone in the asphalt mixture was provided by Bremanger and delivered by Antwerp Stone Terminal (AST). The mixture also contains sand from the Lower-Zeescheldt, of the firm Delahaye – Lauwers. The filler in the asphalt mixture is from Sibelco, a Maastricht based company (Figure 1).

Figure 1. Materials for the manufacturing the bituminous mixture AC 14 base 35/50.

The nanoclay used to modify the bitumen is cloisite-15 from BYK Chemie GmbH. The product consists of bentonite treated with an alkyl group to form an OMMT. The chemical name of this surfactant is: bis(hydrogenated tallow alkyl)dimethyl. It stems from hydrogenated tallow [13, 14, 15]. The nanoclay has an interlayer spacing of approximately 35 Angström. For this study cloisite-15 was chosen to modify the bitumen because of its organic nature and larger interlayer spacing. Additionally, a modification with 3 and 5% nanoclay was chosen as higher percentages could lead to unstable and very viscous bitumen [1]. The auto-ignition temperature of cloisite-15 is 190°C. For this reason, a temperature of 175°C was selected as maximum temperature for the bitumen as well as the granules. To modify the bitumen with nanoclay, a high shear mixer was selected. Using this mixer an intercalated or an exfoliated structure can be obtained [2, 16, 17, 18]. The layer separations in the nanoclay result in higher surface work which intensives the interaction with the asphalt binder (Figure 2).

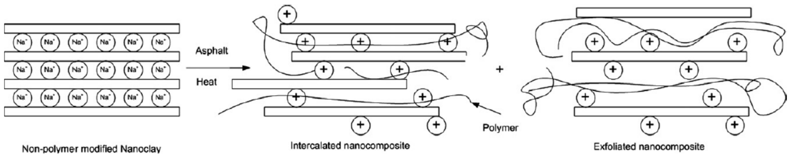

Figure 2. Blended with non-modified and polymer-modified nanoclay. [19]

2.2. Processing/mixing

The modification process was performed on binder batches of approximately 600g. The nanoclay was pre-sieved with a sieve of 0.5mm and dried for 50 min. at 150°C. The bitumen was heated in sealed cans for one hour in a ventilated oven at 150°C. The mixing process can be divided in two stages. At first the nanoclay is pre-mixed with the bitumen. An IKA®RW 16 basic mixer was used with a speed of (400±100) rpm for 10 min. To pull apart the silicate layers a high shear mixer "Silverson L5" was used during the second mixing stage. A detail of the Square Hole High Shear Screen stator is shown in Figure 3. The mixing process was executed at a speed of (4500±100) rpm [2]. In both stages the bitumen was heated on a heating plate at 145°C (Figure 3).

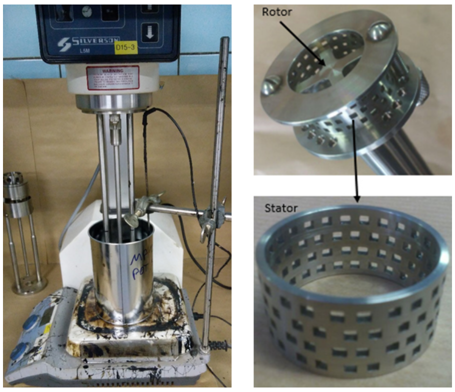

Figure 3. Experimental set-up of the mixing process.

2.3. Experimental setups

2.3.1. Penetration. The penetration is determined in accordance with standard NBN EN 1426 with an Anton Paar automatic penetrometer type PNR12. Immediately after the entire modification process the samples were moulded. Both cooling-down to room temperature as conditioning took 90 min.

2.3.2. Softening point. The softening point is determined in compliance with standard NBN EN 1427 using an automatic appliance by Herzog, type HRB 754. The samples of this test were moulded immediately after the pre-mixing and mixing processes as well. Cooling-down to room temperature took 90 min.; conditioning 15 min.

2.3.3. Fundamental rheological parameters. The complex modulus and phase angle were determined in conformity with standard NBN EN 14770. An Anton Paar DSR type MCR 102 was used. Frequency sweeps were performed at 45°C and ended at -5°C whit temperature steps of 10°C. All samples were moulded immediately after the modification process. Afterwards they were stored in a cold store (5±1 °C) for 20 hours before the test commenced.

2.3.4. Attenuated Total Reflectance – Fourier Transform Infrared spectroscopy (ATR - FTIR). The ATR-FTIR-tests were performed using an Thermo Scientific infrared spectrometer, type Nicolet iS10. The absorption diagram was compiled using OMNIC software based on one reflection of an infrared radiation beam. Before the testing commenced, an environmental scan was carried out. All samples have been examined with 32 consecutive scans with a 4cm-1 resolution [19].

2.3.5. Storage stability. The storage stability is evaluated in accordance with standard NBN EN 13399. The stability is appraised in line with testing the softening point (NBN EN 1427).

2.3.6. ITSR. ITSR-tests are carried out in accordance with standard NBN EN 12697-12. The samples were created manually in keeping with NBN EN 12697 31 and compacted with 25 gyrates in conformity with the Belgian 'Standaardbestek 250' (Version 3.1). The gyrator used is from ELE International, type ELE-Servopac. The measurements (diameter and height) and bulk density of the samples were established in accordance with standard NBN EN 12697-29 and NBN EN 12697-6 (procedure B). The samples were cut perpendicularly on the longitudinal axis having an average height of 41mm and an average diameter of 100mm. The samples were divided into a conditioned and a non-conditioned series (NBN EN 12697-12) to ensure the same average bulk density was reached. To determine the ITSR-level, the samples were tested in compliance with standard NBN EN 12697-23 on their indirect tensile strength (ITS) at a temperature of 20°C. For this a Controls appliance model 82 – P0375 was used. The Uniframe program was used to process the load and deformation data.

2.3.7. Wheel tracking. The creating of the plate samples was in accordance with standard NBN EN 12697-35. A Baustoff-Prüfsysteme Wennigsen GmbH, type GZM-30+ mixing drum was used. The pre-mixing process took 5 minutes. The granulates, filler and bitumen were pre-heated until they reached a pre-mixing temperature of 170°C. A 175°C pre-mixing temperature was determined for the 5% nano-modified mixture because of the increased viscosity. The plates were compacted with a BBPAC mlpc® roller compactor in accordance with standard NBN EN 12697-33 using the high compaction method. Each sample was tested on rutting in accordance with standard NBN EN 12697-22 one week after manufacturing. The standard recommends to test tracking after 30 000 cycles but in this study it was also tested after 40 000 and 50 000 cycles The experimental setup is shown in Figure 4.

Figure 4. Manufacturing and compaction of the asphalt.

3. Results and discussion

3.1. Empirical rheological parameters

The tests show that with an increasing amount of nanoclay the penetration remains consistent while the softening point increases (Table 1).

Table 1. Results of the rheological, penetration & softening point.

	Amount of cloisite-15 (%)		
	0	3	5
Penetration (dmm)			
Before modification	41		
After mixing process	41	42	43
Softening point (°C)			
Before modification	52.2		
After pre - mixing process	52.2	53.3	53.8
After mixing process	52.2	54.0	57.8

The latter is only significant in bitumen with 5% cloisite-15 which can be attributed to the reinforcement effect of the silicate layers on the bitumen. This result could indicate an increased rutting resistance. Subsequently, the penetration and softening point do not change during the modification process which could indicate that the bitumen does not age. Furthermore, the softening point seems to increase after the mixing process in comparison to the pre-mixing process. This result can indicate that an intercalated, possibly exfoliated, structure was obtained.

3.2. Fundamental rheological parameters
The master curves show that a modification with 3% cloisite-15 does not change the fundamental rheological parameters. The with 5% cloisite-15 modified bitumen displays a different behaviour. Namely, for frequencies lower than 0.1Hz, the complex modulus increases. For frequencies, higher than 60Hz the complex modulus decreases (Figure 5a). The phase angle reduces for frequencies lower than 0.1Hz and increases for frequencies higher than 40Hz. The black diagram (Figure 5b) shows that when the amount of nanoclay increases, the bitumen becomes more elastic at a given stiffness. This effect is more pronounced when the complex modulus is lower than 10 GPa.

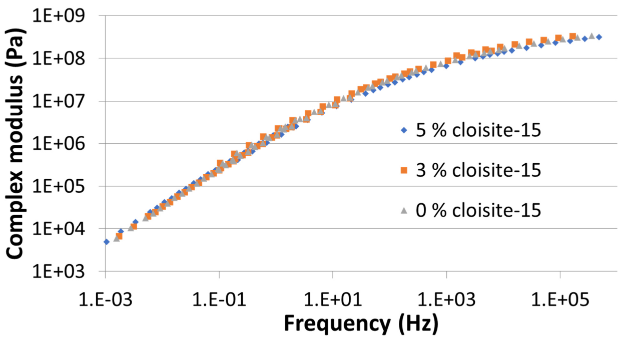

Figure 5a. Master curves (25°C).

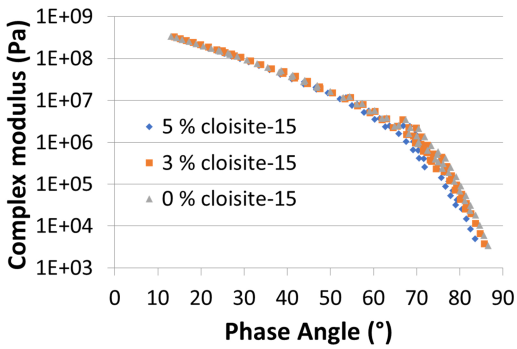

Figure 5b. Black curves.

3.3. ATR - FTIR
The FTIR analysis shows that in modified bitumen (3 and 5%) a greater absorption is perceived around a wave length of 1040cm^{-1} compared to the reference bitumen. This result is attributed to the presence of nanoclay and is related to the amount and the mixing process (complete modification). This could indicate that an intercalated, possibly exfoliated, structure was obtained. An explanation is that after the mixing process the silicate layers remain clustered as a result of which the concentration of cloisite-15 in the bitumen is overall relatively low. Subsequently, the results show that based on the carbonyl bonds (C=0; peak value at 1700cm-1) the bitumen does not age during the modification process.

3.4. Storage stability
After testing the storage stability, the mixtures seemed stable with respect to the sedimentation of silicate layers, because the softening point of the top and bottom of the samples remained almost identical after storage at high temperature. A broader interpretation of the aspect stability could mean that the silicate layers could possibly rearrange themselves when stored at high temperatures resulting in a decrease of interlayer spacing. This will partially undo the positive influence of cloisite-15. This conclusion is reached since the softening point of the modified bitumen (3 and 5%), after storage at high temperature, is reduced to the same value as after the pre-mixing process (Table 2).

Table 2. Results of the storage stability test.

Storage stability	Amount of cloisite-15 (%)		
	0	3	5
softening point (°C)			
Upper part	52.3	53.7	53.4
Lower part	52.4	53.3	53.4

3.5. ITS- and ITSR values

All asphalt mixtures in this work show a resistance against water sensitivity of approximately 70%, no significant changes occur. The ITS curves however, demonstrate that the modified asphalt mixtures (3 and 5%) allow for a greater deformation before the peak load is reached. However, these peak loads are lower compared to the reference mixture. This applies to both the conditioned as the non-conditioned series. Analysis of the fracture surfaces shows that in the samples containing 5% cloisite-15 the fracture pattern is very different compared to other series.

A possible explanation is a lesser internal adhesion between the raw materials which would cause the sample rather to crumble at the edges than a diametric fracture to be formed. The aforementioned ITS curves do not take the volume of the samples into account, therefore the fracture and failure energy was analysed. The fracture energy is virtually the same in all non-conditioned samples. Since the volume of these samples is almost the same and a higher peak load is registered in the reference mixture, the modified samples deform more when the maximum load is reached. The fracture energy in conditioned samples decreases, but because of the high standard deviation, it is difficult to draw a conclusion. The failure energy of the non-conditioned samples remains approximately the same. It follows that the modified samples allow for a slightly larger deformation before failure. For conditioned samples the failure energy increases slightly. It is presumed that the conditioned samples allow for a greater deformation before failure. Based on the standard deviation, this conclusion needs to be taken with caution. The results presented above follow the hypothesis that the failure mechanism of modified samples may differ due to reduced adhesion. Subsequently it is stated that the modified samples can deform more before failure because of the reinforcement effect of nanoclay. The mixture bonds better in its entirety even though the bitumen's adhesion is reduced.

3.6. Wheel tracking

The tested AC 14 base 35/50 mixture for base layers already has an excellent rutting resistance, therefore only marginal changes were detected in the modified mixtures. The with 5% nanoclay modified mixture is the only one that shows visible improvement.

From the beginning the rut depth is less in comparison to both other mixtures. The rut depth at 30 000 cycles is 2.4% which in absolute numbers is a small change. This compares to an improvement in rutting resistance of on average 15%, which is relatively speaking a strong improvement. Even after 50 000 cycles the improvement remains visible in mixtures with 5% nanoclay. There is still some space for

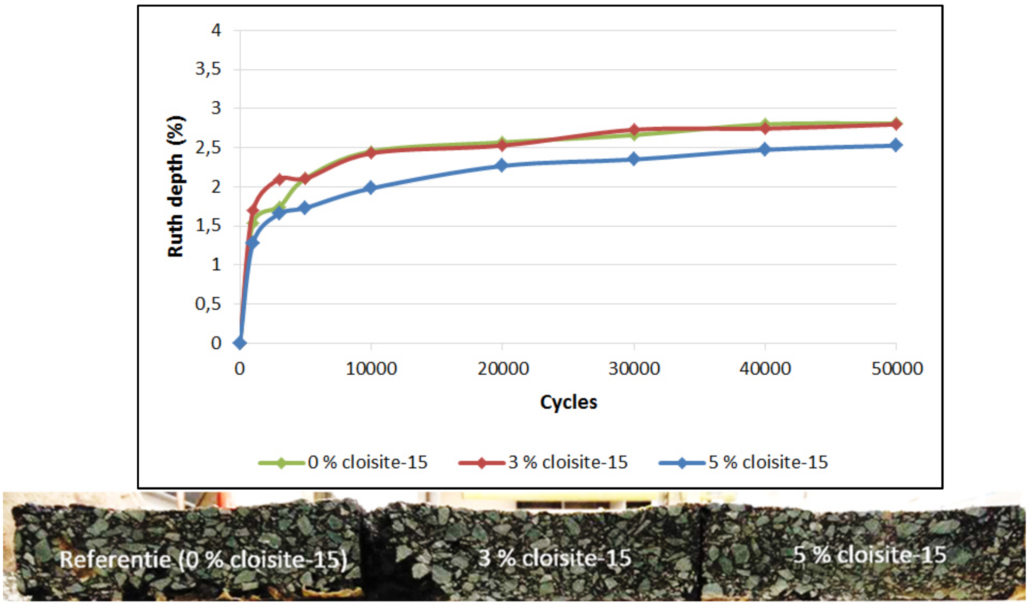

Figure 6. Deformed asphalt slabs after wheel tracking experiment.

4. Conclusions

In generall, nanoclay seems to have a slightly positive influence on durability properties in asphalt for base layers. Essential to this is the intercalated structure that might be obtained which was proved by the FTIR. The softening point increases when the amount of added nanoclay is increased, which can be attributed to the reinforcement effect of nanoclay. The penetration however remained consistent when nanoclay was added. A possible explanation for this latter, is that the bitumen is already so hard that the added nanoclay has no effect on the penetration value. In bitumen modified with 5% nanoclay, a slight increase of stiffness and elasticity takes place at low frequencies. It is not a significant increase according to which a modification of a relatively hard bitumen with nanoclay may not be efficient. Cloisite-15 seems to have good storage stability in the bitumen. In the broader interpretation of this notion, the silicate layers seem to have the ability to rearrange themselves at high temperatures so that the reinforcement function of nanoclay is nullified. It appears that cloisite-15 modified bitumen should be processed into asphalt in a relatively short period of time. The water sensitivity remains consistent whereas the rutting resistance increases slightly when bitumen is modified with 5% nanoclay. There is a limited influence, which is why the modification of existing asphalt mixtures for base layers in higher construction class is less recommended. The ITS value of nanoclay decreases, which can be explained by a reduced adhesion in modified asphalt mixtures. It is therefore important to determine the optimum binder content in order to obtain an equal bonding characteristic in modified asphalt mixtures. Nanoclay does seem to provide a better reinforced asphalt structure. For fatigue properties in asphalt mixtures, this can be positive.

Overall, based on this study, two research paths are recommended. Firstly, it is recommended to make a comparison between an existing asphalt mixture and this asphalt mixture with a softer bitumen that is modified with nanoclay. Secondly, it is recommended to conduct research into the use of nanoclay in top layers. Mixtures for top layers more often contain a softer bitumen which can lead to the positive effects of the nanoclay being more pronounced. Furthermore, the aging resistance can increase because of the barrier properties. In addition, this research shows that rutting resistance can increase through modification, which is of great importance for the durability properties of top layers.

Acknowledgements

The authors would like to thank the "Energy & Materials in Infrastructure & Buildings" (EMIB) research group, University of Antwerp, and Hilde Soenen of Nynas to make this research possible.

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