Introducing a nitrogen conditioning to separate oxidative from non-oxidative ageing effects of hot mix asphalt

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Bitumen used as a binder is subjected to ageing that leads to increased stiffness and brittleness. For the simulation of long-term ageing of hot mix asphalt (HMA), most methods are based on conditioning at high temperatures to increase oxidation. This paper investigates the impact of non-oxidative / thermal and oxidative effects on long-term ageing of asphalt mix specimens in the laboratory and aims at separating these effects. Therefore, specimens are placed in a heating cabinet at different temperatures ranging from +60°C to +160°C. One part of the specimens is exposed to the air atmosphere, while the other part is stored under nitrogen atmosphere (N-VAPro). Thereby, oxidative ageing is avoided for the nitrogen-stored specimens and the combination of thermal effects can be separated from oxidative effects. The changes in the material behaviour of HMA as a result of the different ageing regimes are investigated by stiffness tests at intermediate temperatures. Furthermore, Dynamic Shear Rheometer (DSR) tests are carried out on virgin, aged binder (RTFOT, RTFOT + PAV) as well as on recovered bitumen of both conditioning groups. The results indicate that conditioning temperatures must be kept below 110°C to prevent the asphalt mixtures from non-oxidative ageing effects. However, atmospheric air conditioning for HMA specimens is only suitable as a long-term ageing procedure for temperatures above 110°C to increase the oxidation rate to an efficient rate. This threshold temperature can also be seen as the limit value for lab-ageing procedures that should not be exceeded to avoid non-oxidative ageing effects that cannot occur in the field due to limited maximum temperatures. Furthermore, a double exponential increase with the ageing temperature on the binder level was shown.

Keywords: hot mix asphalt; long-term ageing; oxidative ageing; nitrogen storage; thermal ageing; non-oxidative effects

1. Introduction

Bitumen as an organic material is subject to changes in its behaviour throughout its life by a combination of several chemical and physical processes that are triggered by temperature. In pavement engineering, ageing of bitumen and bituminous bound pavements is divided into short-term ageing (STA) in the process of hot mix asphalt (HMA) production and compaction within a few hours and long-term ageing (LTA) of a pavement during its in-service life within years. Both ageing steps are a combination of the general ageing effects oxidation, volatilisation, steric hardening and polymerisation (Masson, Collins, & Polomark, 2005; Traxler, 1961). STA is triggered by fast oxidation due to high temperatures and a high specific surface, as well as a physical effect, where remaining volatile components may evolve from the bitumen (non-oxidative,

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thermal effects) (Baek, Underwood, & Kim, 2012; Hofko et al., 2017; Petersen, 1994; Steiner, Maschauer, & Hofko, 2018). LTA is driven by slow oxidation especially of the upper pavement layers by oxidant gases available in the atmosphere (e.g. ozone, nitric oxides) and UV radiation (Menapace & Masad, 2018; Morian, Hajj, Glover, & Sebaaly, 2011). Bitumen becomes stiffer and more brittle and thus, pavements are more prone to failure by low temperature and fatigue cracking with increasing ageing of the binder (Eberhardsteiner & Blab, 2017; Farrar, Hajj, Planche, & Alavi, 2013; Mogawer et al., 2015; Steiner, Hofko, Dimitrov, & Blab, 2016; Teshale, Moon, Turos, & Marasteanu, 2011). Since bitumen ageing affects durability and recyclability of pavements crucially, it is important to assess ageing behaviour and resistance to ageing of binders and mixtures at the stage of mixture optimisation to achieve cost- and energy-efficient pavements with low maintenance demands, a long service-life and high recycling potential.

To assess bitumen ageing in the laboratory within an efficient amount of time, the rolling thin film oven test (RTFOT) (ASTM, 2012; CEN, 2007a) and the pressure ageing vessel (PAV) (Airey, 2003; ASTM, 2013; Behera, Singh, & Amaranatha Reddy, 2013; CEN, 2012; Mallick & Brown, 2004) are standardised and widely accepted methods to transfer virgin binders into the state of STA (RTFOT) and LTA (RTFOT + PAV).

HMA ageing procedures could assist in analysing changes of HMA material behaviour due to ageing from changes of binder behaviour. More than 30 laboratory-ageing procedure of loose or compacted asphalt mix have been developed in the last decades (C.A. Bell, AbWahab, Cristi, & Sosnovske, 1994; Çetinkaya, 2011; Maschauer, Steiner, Mirwald, Hofko, & Grothe, 2018; Partl et al., 2013; Porot & Bobrisow, 2008; D. Steiner et al., 2016; Yin, Arámbula-Mercado, Epps Martin, Newcomb, & Tran, 2017). Most of these methods have to be seen as critical since conditioning temperatures exceed values that usually occur in surface layers of pavements. Commonly used temperatures are +100°C (Bell, Sosnovske, & Wieder, 1994; Çetinkaya, 2011) and +135°C (Potschka & Tappert, 1987; Poulikakos et al., 2014). Thus, additional non-oxidative effects due to higher temperatures (e.g. vaporisation of further volatile binder components) could be activated that cannot occur in the field. Some other recently developed LTA procedures use an alternative approach in keeping the temperatures in realistic areas (+60°C) and maximise the presence of the highly oxidant gases that are present in the field. Therefore, these gases are responsible for the oxidation of the binder. This is the only way to achieve an acceleration of the chemical reaction instead of increasing the temperature or the pressure (D. Steiner et al., 2016) used this approach.

To better understand, how important it is to choose the right parameters for an LTA method, a short excursus to fundamental rules of chemical reactions is given based on the collision theory by Trautz (1916). The speed of chemical reactions (successful collisions) is linked to the following parameters:

- Increasing the particle concentration, increases the likelihood that successful collisions take place.
- Since a certain activation energy is necessary for reactions, increasing the temperature accelerates the particles speed and increases the reactions.
- Increasing the pressure leads to a higher particle concentration and therefore a higher reaction speed.

According to Vant’hoff (Benedix, 2011; Hoff, Cohen, & Ewan, 1896), the “Reaktionsgeschwindigkeit-Temperatur” R.G.T rule (reaction rate temperature rule) says that with a temperature increase of 10 K, the rate of chemical reactions is increased by the factor two to three. This rule was further developed by Arrhenius to the Arrhenius equation (Arrhenius, 1887). Hence, ageing temperatures have exponential correlations to the laboratory ageing of bituminous materials.
Looking now at viscoelastic behaviour of bituminous materials, it is obvious, that the viscosity is also exponentially correlated to temperature. Similarly to temperatures at chemical reactions, the Arrhenius equation can be applied to correlate temperature und viscosity (García-Morales et al., 2004). Binders exhibit lower viscosity at higher temperature. Increasing temperatures for simulating ageing in the laboratory means that due to the lower temperatures thin bitumen films can flow more easily. Therefore, the surface of these thin bitumen films that are attacked by reactive oxygen species (ROS) can be renewed faster and ageing processes are increased. Simone, Pettinari, Petretto, and Madella (2012) and Anderson and Bonaquist (2012) showed the influence of viscosity on ageing susceptibility and presented an equiviscosity concept. According to Petersen (2009), the temperature sensitivity is linked to two independent effects, the above mentioned R.G.T rule and a physicochemical effect, that the microstructure is disrupted and broken up. The superimposition of increasing velocity of chemical reactions at higher temperature and a simultaneously reduce of the viscosity at higher temperatures can lead to enormous increases of ageing effects. Hence, the authors are of the opinion that increasing temperature at the laboratory ageing can lead to doubled exponential changes of the binder properties. Therefore, ageing bituminous materials at equiviscous conditions (temperature and pressure) should be the aim.

2. Approach and objectives

The main objective of this paper is to develop a conditioning method for compacted HMA samples to analyse effects of temperature on thermal/non-oxidative and oxidative LTA ageing. Therefore, nitrogen is used to prevent oxidative ageing effects from the HMA samples. The method can be seen as an expansion of VAPro (Viennese Aging Procedure) (D. Steiner et al., 2016). In combination with nitrogen, the method is called N-VAPro throughout this paper. Additionally, samples are conditioned in atmospheric air at the same temperatures to separate thermal / non-oxidative from oxidative effects. Similar studies for STA for binder in the laboratory have been carried out with Nitrogen Rolling Thin Film Oven Tests NRTFOT by Parmeggiani (2000). Preliminary analysis of non-oxidative effects at LTA procedures was carried out by an ageing study at TU Wien (D. Steiner et al., 2016). HMA specimens were placed under nitrogen atmosphere at + 75°C for 4 days. The results showed that no thermal effects could be observed at this temperature. The ageing level of the extracted bitumen was comparable with RTFOT-aged bitumen. The newly developed method presented in this paper should be used in an ageing study to give a better understanding of parameters for LTA HMA ageing in the laboratory. The results should be used to recommend ageing temperature limits for laboratory LTA of HMA.

To give a basis for selecting the ageing temperatures for this study, the authors studied ageing-related temperature recommendations, given in the literature. First of all, it is important to know the possibly highest temperatures that can occur in the field and can serve as the lower benchmark. For moderate climates, surface temperatures of HMA layers reach up to 65°C (Hofko et al., 2014) during summer season. At this temperature, no volatilisation should occur. Following statements related to possibly upper benchmark of ageing temperatures are given in the literature:

- According to Mill, Tse, Loo, Yao, and Canavesi (1992), no chemical changes are observed at 60°C–130°C in the absence of oxygen, although small amounts of volatiles may be lost at elevated temperatures. Above 150°C, non-oxidative reactions may begin to cause chemical changes, even without oxygen.
- Read and Whiteoak (2003) stated that the loss of volatiles starts at 150°C and is doubled with an increase of 10–12°C.
- Sulfoxide decomposition and the disruption of polar molecular associations starts at temperatures that exceed 100°C (Petersen, 2009).
Most recent studies recommend reducing the oven ageing temperature to 95°C, even if it
takes up to 10 days to achieve an ageing level that matches 4 years of field ageing at 6 mm
below the pavement surface. Contrary to ageing at 135°C, the relationship between binder
chemistry and rheology is unaffected by the ageing temperature (Transportation Research
Board & National Academies of Sciences, & Medicine, 2017).

3. Materials, test methods and experimental programme

3.1. Experimental programme and course of the research project

Figure 1 provides an overview of the test programme. During the course of the project, two
development phases of the method were needed and resulted in two different conditioning setups.
To get an idea about the nitrogen storage of HMA samples, the study looked into the impact
of temperature on ageing by comparison with atmospheric air-stored specimen. Atmospheric
air ageing / storage is a widely used method for ageing loose / compacted asphalt mixes for
simulating the STA as well as LTA. Thereby, temperature varies in a broad range. Therefore, it
is important to understand how the nitrogen storage performs related to these standard methods.
To get a complete view, tests on four to five different temperatures ranging from +60°C to
+160°C were initially planned. The results should give an overview of the expected increase
of the dynamic modulus $|E^*|$ and decrease of the phase angle of HMA and the dynamic shear
modulus $|G^*|$ and phase angle of the recovered binder considering non-oxidative and oxidative
effects.

Furthermore, the dynamic shear modulus $|G^*|$ of the same virgin, RTFOT + PAV-aged binder
were compared with the data of the recovered binder from aged HMA specimens.

After the first development of the experiment setup and while carrying out the first experimen-
tal test schedule, some problems with the N-VAPro storage occurred at the higher temperatures
($>135°C$). Therefore, a redesign of the setup was needed and the test programme was repeated
with using a different binder. Detailed descriptions of the setup is given directly in the chapter
“development of the N-VAPro aging method”. In order to show the possibilities of the condition-
ing method N-VAPro, all test data from develop stage I are shown in this paper. A binder from
different origin was used and therefore a broader spectrum of insights is given. The conditioning
time, using binder II was reduced from 4 to 3 days. The reason for this, as VAPro was continu-
ously improved, the standard ageing time has been reduced. To ensure a good comparability, the
conditioning time for N-VAPro was also reduced.

3.2. Materials

For the presented study, an asphalt concrete with a maximum nominal aggregate size of 11 mm
(AC 11) was employed. As a binder two (I/II) unmodified 70/100 pen (PG 58-22/91 pen and PG
64-22/79 pen) were used. The main characteristics of the binder are listed in Table 1.

The binder content was set for both mixtures (binders I and II) to 5.2% by mass with a target
void content of 7.0% by volume. The grading curve is shown in Figure 2. Furthermore, the upper
and lower limit grading according to national specifications (ONI, 2009) are illustrated.

3.3. Specimen preparation

The mixture was prepared in a laboratory reverse-rotation compulsory mixer, according to EN
12697-35 (CEN, 2007c), with a mixing temperature of $+170°C$. HMA slabs ($50 \times 26 \times 4$ cm)
were compacted in a roller compactor according to EN 12697-33 (CEN, 2007b). From the slabs,
eight specimens are cored with a diameter of 100 mm. The air void content of the specimens used
Figure 1. Flow chart of the experimental programme.

For the test programme range from 6.6 to 8.3% by volume for mixture I and from 5.9 to 8.0% by volume for mixture II.

For bitumen testing, bitumen was extracted according to EN 12697-3 (CEN, 2013) with tetrachloroethylene (C₂Cl₄) as a solvent. The solvent-bitumen solution was distilled according to EN 12697-3 (CEN, 2013) to recover the binder samples (Hospodka, Hofko, & Blab, 2017).
Table 1. Binder characteristics.

| Parameter                               | 70/100 pen (I) | 70/100 pen (II) |
|-----------------------------------------|----------------|-----------------|
| Penetration (1/10 mm)                   | 91             | 79              |
| Softening Point Ring and Ball (°C)      | 46.8           | 47.2            |
| SHRP Performance Grade (°C)             | 58-22          | 64-22           |

3.4. Dynamic modulus testing of HMA

Cyclic indirect tensile tests (CIT-CY) were carried out on all specimens before and after ageing at a temperature of $+10^\circ$C and frequencies ranging from 0.1 to 20 Hz by applying a sinusoidal load. From test data the dynamic modulus $|E^*|$ and the phase angle $\varphi$ can be determined to describe the viscoelastic behaviour of the specimen (Di Benedetto, Partl, Francken, & De La Roche Saint Andre, 2001). In a series of pre-tests, the upper stress level of the sinusoidal load was determined so that the elastic horizontal strain amplitude of the specimen during testing is between $4.5 \times 10^{-2}$ m/m and $5.5 \times 10^{-2}$ m/m. This is necessary for repeated testing to prevent the specimens from suffering permanent deformation. It was shown that repeated tests on the same specimen are possible with these loading conditions (Steiner, Hofko, & Blab, 2016). This is a necessary precondition since all specimens were tested twice, before and after laboratory ageing. To avoid differences in the performance characteristics due to the compaction direction (Hofko, Blab, & Alisov, 2016), the slabs were marked with lines before the specimens were cored out. All specimens were tested exactly in compaction direction both times.

3.5. Dynamic shear modulus of bitumen

Dynamic Shear Rheometer (DSR) tests were carried out on bitumen samples recovered from all laboratory-aged (N-VAPro vs. atmospheric air) HMA specimens. The test conditions were chosen according to the SHRP procedure (Petersen et al., 1994) and EN 14770 with a temperature sweep from $+46^\circ$C to $+82^\circ$C using the large plate (diameter: 25 mm) and a 1 mm gap. The testing temperature was controlled stepwise using 6°C steps. A frequency of 1.592 Hz is employed. From the test data, the dynamic shear modulus $|G^*|$ and the phase angle $\delta$ vs. frequency are determined.
3.6. Development and modifications of the N-VAPro method

The setup and equipment which was used for the conditioning procedure for BINDER I is based on the VAPro – Viennese Aging Procedure (Frigio, Raschia, Steiner, Hofko, & Canestrari, 2016; D. Steiner et al., 2016). HMA specimens are assembled within a triaxial cell between filter stones and are covered by an elastic membrane. The triaxial cell is located in a heating cabinet with sealed inlets, where the temperature was varied for the experimental run for a conditioning duration of 4 days. The complete system was flooded with nitrogen for a few minutes to expel any atmospheric air. An overpressure of 50 kPa was applied within the triaxial cell. The specimens were also flown through with nitrogen for a few minutes to saturate all air voids. The flow pressure was set to 25 kPa. Due to the higher lateral pressure, the elastic membrane is pressed onto the specimen surface and the gas is forced to flow through the specimen, instead of passing on the outside. After flooding with nitrogen, all inlets were closed to retain the nitrogen within the pressure cell and specimen.

After the first ageing study of binder I, it turned out that the setup is prone for damages. It consists of a plastic cylinder that is not temperature resistant above 110°C. Therefore, the cylinder was replaced with glass cylinder. This, in turn, sealed with metal adapters with a slight pressure in the axial direction can quickly lead to cracks in the glass cylinder. Another problem has been encountered with the sealing membrane within the pressure cell. At temperatures above 120°C, the membrane is hardly separable from the aged specimens. Both difficulties could have influenced the results at 135°C N-VAPro ageing in the first stage.

To overcome these downsides of setup I, an alternative approach was developed to carry out ageing on specimens from binder II, which is shown in Figure 3. A pipe clamp (DN = 100 mm) was used to seal the specimens on the lateral surface. HMA specimens are also assembled in a row between filter stones and two endplates. The pipe clamp can be perfectly fitted to the specimen dimensions. This equipment is more durable for conditioning or ageing tests with a forced gas flow at temperatures far higher than +100°C. In this stage, the specimens were continuously flown through with nitrogen for an ageing duration of 3 days. In general, conditioning under nitrogen atmosphere is supposed to prevent any oxidative ageing and thus, only trigger non-oxidative effects.

In a next step, three HMA specimens were placed in the atmospheric air of the heating cabinet at each selected ageing temperature for 4 (binder I) or 3 (binder II) days. This time the heating

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Figure 3. Improved Setup II for N-VAPro tube clamp ageing – BINDER II.
cabinet was equipped with a forced convection. The HMA specimens are exposed to all ROS, which are present in the atmospheric air. This leads to different chemical processes (e.g. oxidation) at the varied temperatures compared to storing the specimens in an inert gas atmosphere. To maintain its proper shape, the specimens are positioned in metal moulds and wrapped with silicone foil as a release layer. Atmospheric air ageing is supposed to trigger both, oxidative, as well as non-oxidative / thermal ageing effects.

By comparing results from specimens and recovered binders subjected to N-VAPro and atmospheric air ageing, non-oxidative and oxidative ageing effects can be separated.

4. Discussion and laboratory test results

4.1. Dynamic modulus of HMA

In the first development stage of N-VAPro, HMA specimens were subjected to atmospheric air ageing and N-VAPro conditioning at 4 (N-VAPro) / 5 (atmospheric air) different temperatures (60°C, 85°C, 110°C, 135°C and 160°C). The specimens were tested for their viscoelastic behaviour (dynamic modulus $|E^*|$ and phase angle $\phi$) in the CIT-CY at $+10^\circ$C and frequencies ranging from 0.1 Hz to 20.0 Hz. All specimens used for the study were tested twice, before and after ageing to directly compare changes in its behaviour due to the different ageing methods. In order to make the figures more legible, the results are only shown for testing frequency 5 Hz. All frequencies show similar trends with conditioning and ageing. The results of the stiffness testing are shown in Figure 4. The diagram shows the relative change in dynamic modulus $|E^*|$ of the same specimen in aged condition vs. unaged condition over the temperature range for both ageing methods. The data presented in the diagram are a collection of the single values and the mean values (MVs). Furthermore, the standard deviation for three single tests of each temperature is stated. To give a magnitude of the significance due to ageing, a liability range for the repeated CIT-CY testing is shown. Steiner, Hofko, and Blab (2016) analysed the possible increase of stiffness with 5% by testing the same specimen twice. Therefore, an increase of more than 5% can be seen as significant due to ageing.

For both conditioning methods, an exponential increase of the dynamic modulus $|E^*|$ can be observed with increasing temperature. For the atmospheric air ageing, significant changes can be
seen at temperatures of +85°C and higher. Comparing that with N-VAPro ageing, it can be seen that significant changes start with ageing temperatures of +135°C. Looking at the regression of the atmospheric air ageing, the coefficient of determination $R^2$ is equal or above 0.96, which indicates an excellent correlation of dynamic modulus vs. ageing temperature with an exponential regression. At +135°C for N-VAPro, the limit of the testing device was reached. Therefore, these results have to be looked at with caution. Nevertheless, the results are significant lower than with atmospheric air ageing at the same temperature. With a fully functional equipment, the increase of dynamic modulus $|E^*|$ should be lower. Therefore, the exponential regression could be a misapplication, even if the coefficient of determination $R^2$ are in an acceptable range of 0.68 or higher.

The results of the phase angel $\varphi$ are shown in Figure 5. The diagram shows the change in phase angle $\varphi$ of the same specimen in aged condition subtracted by the unaged condition over the temperature range for both conditioning methods. The data presented in the diagram are a collection of the single values and the MVs. Furthermore, the standard deviation for three single tests of each temperature is stated. To give a magnitude of the significance due to ageing, a liability range for repeated CIT-CY testing is shown. Steiner, Hofko, and Blab (2016) analysed the decrease of the phase angle $\varphi$ with 2.2° by testing the same specimen twice. Therefore, a decrease of more than 2.2° can be seen as significant due to ageing.

Looking at the results of the first stage of the paper using binder I, similar trends related to the dynamic modulus $|E^*|$ can be seen. Unlike the evaluation of the regressions for dynamic modulus $|E^*|$, the authors have declined to run regression analysis for N-VAPro, due to the previously mentioned issues at 135°C. For the atmospheric air ageing, a different approach of analysing the regression has been chosen. At a first sight, an exponential regression can be determined. In variation from this, it was analysed if two partial linear regressions will fit the results. It is based on a hypothesis that ROS are hardly reactive at intermediate temperatures and the oxidative ageing will start drastically at a certain temperature using atmospheric air. Looking at the coefficient of determination $R^2$ is equal or above 0.98, which indicates an excellent correlation of phase angel vs. ageing temperature with linear regression. Considering the previously indicated threshold for significant changes due to conditioning, it can be seen that the results of the phase angle did not exceed –2.2°. Significant changes start at 85°C using the atmospheric air ageing method. Using N-VAPro, significant changes can only be seen at 135°C, whereby 135°C in turn have to be seen critical.
In the second development stage of N-VAPro, HMA specimens were subjected to atmospheric air conditioning and N-VAPro ageing at four different temperatures (60°C, 85°C, 110°C and 135°C). The results of the stiffness testing are shown in Figure 6. The diagram shows the relative change in dynamic modulus $|E^*|$ of the same specimen in aged condition vs. unaged condition over the temperature range for both ageing methods.

In this stage of the paper, using an enhanced setup for the N-VAPro method, a different course of the results with temperature can be seen. With increasing temperature, the dynamic modulus is not increasing as much as in the first stage using binder I. Therefore, a different regression was used to fit the results of the N-VAPro samples. Instead of using an exponential regression, a logarithmic fit was applied. Comparing both methods, it can be seen that with N-VAPro ageing significant changes starts already with ageing temperatures of $+85°C$ for this binder. For atmospheric air ageing, significant changes can be seen at all temperatures and the increase of stiffness is always significant higher than for N-VAPro ageing. Looking at the regression of the atmospheric air ageing, the coefficient of determination $R^2$ is equal or above 0.96, which indicates an excellent correlation of dynamic modulus vs. ageing temperature with an exponential regression. The new applied logarithmic regression fit the results perfectly, taking into account that the coefficient of determination $R^2$ is 0.98, which suggests that it is validly using this regression.

The results of the phase angle $\varphi$ of the second stage using binder II and the enhanced N-VAPro setup are shown in Figure 7. The diagram shows the change in phase angle $\varphi$ of the same specimen in aged condition vs. unaged condition over the temperature range for both ageing methods.

Looking at the results of the second stage of the paper using binder II similar trends regarding the course of the results can be seen, but shifted to lower temperatures. Significant changes due to ageing occurred at $+85°C$ for atmospheric air ageing and at $+110°C$ for N-VAPro ageing. A substantial difference here is that a starting point of ageing (intersection of regression lines) cannot be seen. It is likely, that binder II is more susceptible to ageing and therefore the starting point of ageing is already at $+60°C$. If more tests at temperatures below $+60°C$ would be carried out, a kink of the regression lines could possibly be seen.

As an analogy to the increase of the dynamic modulus $|E^*|$, the course of the N-VAPro results is different. Due to the enhanced setup, the ageing at 135°C is not as high as in the first stage. Therefore, an exponential or linear regression cannot be applied to the results. More precisely,
a logarithmic regression fits the results best. Looking at the goodness of fit, the coefficient of determination \( R^2 \) are equal or above 0.99, which indicates a perfect correlation of phase angle vs. ageing temperature with linear regression at atmospheric air ageing. The coefficient of determination \( R^2 \) for N-VAPro conditioning is 0.94 and therefore a logarithmic regression describes the correlation between temperature and decrease of phase angle perfectly.

Achieving a better comparability of both research stages / setups / used binder, the results are gathered and compared in this section within a few figures. To better understand which effects can have influenced the results, a list of possible influences is compiled:

- As written previously, testing the same specimen twice, before and after ageing, requires to know the possible change of the dynamic modulus \( |E^*| \). Therefore, results of specimens tested twice without ageing in between were collected in Steiner, Hofko and Blab (2016). A possible increase of \( |E^*| \) was calculated with 1.05. All increases above this threshold can be seen as significant.
- Similarly, the phase angle has to decrease more than 2.2° to ensure significant changes.
- The storage of compacted HMA specimens can lead to re-densifications. Taking into account that standard compaction temperature are above 120°C and mechanical compaction energy is additionally loaded by heavy machines, it can be assumed that hardly any effects will occur at 110°C and lower. Since there is no loading during the ageing procedure, re-densification at 135°C is as well unlikely. Only at temperatures of 160°C, densifications of the specimen can happen. Should there be influences, it could can be back calculated with results from the recovered binders.

The following analyses were carried out:

- The changes in the mechanical properties are separated in non-oxidative effects and oxidative effects. The difference of atmospheric air-stored specimens vs. N-VAPro aged specimens can only be oxidative effects due to the agents in the atmospheric air.
- If re-densification effects exist, the influence for the amount of oxidative ageing is eliminated, since these effects have to take place at both ageing methods. Only the amount of non-oxidative ageing can imply re-densifications. However, for lower temperatures only physical effects as volatilisation should take place.
To achieve the true increases of only significant ageing effects the values were reduced by the calculated possible effects of testing the specimens twice. Thus, $|E^*|_{\text{aged}}/|E^*|_{\text{unaged}}$ was reduced by 1.05. The decrease of the phase angle $\varphi_{\text{aged}}-\varphi_{\text{unaged}}$ was reduced by 2.2°.

The results of the calculated and compared results for the dynamic modulus $|E^*|$ are shown in Figure 8. The x-axis shows the ageing temperatures, while on the y-axis the significant change of $|E^*|$ is shown. Figure 8 (left side) comprises the first stage using binder I with an ageing duration of 4 days. Figure 8 (right side) comprises the second stage using binder II with an ageing duration of 3 days. Even though the ageing duration for the second stage and binder II is shorter, the observed increase of the stiffness is higher than for binder I. Oxidative ageing effects start at temperatures of $+60^\circ$C, while for binder I these effects take place slightly at $+85^\circ$C but starting at $110^\circ$C. Taking into account that N-VAPro ageing for binder I at $+135^\circ$C can be seen critical, the amount of non-oxidative effects can be overestimated. The total increase for oxidative effects is true, but the share can be different. Looking at non-oxidative effects, hardly any increases can be seen at binder I. At binder II, already at $+85^\circ$C non-oxidative effects like volatilisation can be seen. Generally, it can be assumed that binder II is more susceptible for ageing for both ageing methods than binder I.

Looking at the results of the phase angle $\varphi$, it is even more clearly visible than for the stiffness results that binder II is more prone to ageing. For binder I, almost no or hardly any significant ageing effects can be seen for temperatures of $+110^\circ$C and lower. First major changes can be identified at $135^\circ$C, although here again the share of the non-oxidative effects has to be seen as critical. At binder II, significant non-oxidative effects start with temperatures of $+85^\circ$C and higher (Figure 9).

### 4.2. Dynamic shear modulus

To investigate potential non-oxidative effects from temperature, bitumen from all N-VAPro and atmospheric air-stored samples were extracted and recovered from the HMA. Analysis of changes of the viscoelastic behaviour was carried out. In addition, STA bitumen by RTFOT and LTA bitumen by RTFOT + PAV were tested as well to compare standardised bitumen ageing procedures to the presented procedures.

Since HMA ageing is mainly influenced by binder ageing, an analysis of the recovered binder samples gives a broader perspective and substantiate the results.
The results of the DSR stiffness testing are shown in Figures 10 and 11 (left side). The diagrams show the relative change in dynamic modulus $|G^*|$ of the binders in aged condition vs. unaged condition over the temperature range for both ageing methods. The data presented in the diagram are a collection of the single values and the MVs. Furthermore, the standard deviation for three single tests of each temperature is stated for binder II. Binder I was recovered as a composite sample of more HMA specimens for one ageing method and ageing temperature. The samples of binder II at $+85°C$ N-VAPro ageing could not be analysed at the binder level due to equipment failure during the recovering process. Since there was a limited stock of materials, further specimens could not be produced to repeat these samples.

The dotted lines represent data from the RTFOT and RTFOT + PAV-aged bitumen. At the binder level, the results of binder I as well as binder II indicate no significant changes in the mechanical behaviour for the N-VAPro samples below $+110°C$. At $+135°C$, $|G^*|$ significantly increased for both binders in the nitrogen atmosphere. If it is assumed that the mechanical
changes at the temperatures of +110°C and below are only due the STA at the slab production, we can suggest that ageing effects, which can be attributed to non-oxidative ageing, are starting at temperatures between +110°C and +135°C. Between +60°C and +110°C, all binders are 2.0–3.2 times stiffer than the virgin binder, whereas the +135°C nitrogen samples are 4.0 and 4.1 times stiffer.

Since hardly any changes can be seen at +110°C and below for the N-VAPro method, a regression analysis was not carried out. For the atmospheric air ageing methods, an exponential increase of the dynamic modulus $|G^*|$ can be observed with increasing temperature. Unlike to the asphalt results, it was not possible to fit the data with a simple exponential regression. Therefore, a more comprehensive function was applied. This reflects combination of the effects described in chapter I with increasing velocity of chemical reactions at higher temperature and a simultaneously reduce of the viscosity at higher temperatures. These superimposition leads to progressive increases. Furthermore, the atmospheric air ageing shows significant changes at temperatures of +85°C and higher. Comparing that with N-VAPro ageing, it can be seen that significant changes starts with ageing temperatures of +110°C. At +135°C the limit of the testing device was reached, as previously described. Nevertheless the results are significant lower than with atmospheric air ageing at the same temperature. Additionally, a further data point was added to the figure, which was not part of the test programme of this paper. D. Steiner et al. (2016) used the same binder and setup as it was used in the first stage. It is shown that similar trends occur.

The analysis of the phase angle $\delta$ shows a similar picture as the dynamic modulus $|G^*|$ evaluation. The results of the DSR phase angle $\delta$ are shown in Figures 10 and 11 (right side). Changes due to the ageing are shown by subtracting the phase angle in aged condition from the phase angle in virgin condition. Therefore, this leads to the decrease of the phase angle due to ageing.

The summarised results and compare both stages of the paper using different setups and binders, resuming figures are shown in Figure 12. It shows the mean values of the relative change in dynamic shear modulus $|G^*|$ from recovered bitumen samples vs. virgin bitumen. Additionally, thresholds are shown using RTFOT and RTFOT + PAV-aged bitumen. Using the data from
Figure 12. Change in dynamic shear modulus $|G^*|$ of bitumen recovered from lab-aged HMA specimen (4 days binder I – 3 days binder II) to virgin bitumen sample.

both ageing methods allows to separate the different ageing effects as it was done in the dynamic modulus $|E^*|$ evaluation for HMA testing. Since the unaged stage of the binder is the virgin binder, it has to be assumed that the ageing increases are different for mix and binder level. For HMA at the “unaged stage”, the samples have already received as STA due to the mixing and compaction. That is not the case for the binder analysis. Therefore, the non-oxidative ageing categories comprises as well this STA.

It is clearly recognisable that binder II is more prone to ageing than binder I. Even if it is considered that in the first stage a longer ageing time (4 vs. 3 days) was used. Looking at the data from the atmospheric air-aged samples, almost no effects occur until $+85^\circ\text{C}$. Starting at $+110^\circ\text{C}$ significant changes can be seen. The oxidative species of the atmospheric air are reactive enough to trigger oxidative ageing only above this temperature. The difference between N-VAPro-stored and atmospheric air-stored samples can be attributed to oxidative LTA effects.

5. Conclusions and outlook

5.1. Conclusions

The main drive for the research study presented within this paper is to provide a better understanding of parameters for LTA of HMA ageing in the laboratory. Ageing methods on mix level can bring additional benefit in assessing binder for construction projects, beside the standardised bitumen ageing methods such as RTFOT and PAV. Choosing these method parameters correctly is not always an easy task, since the mechanical and ageing behaviour of bitumen is highly complex. Different bitumen grades and provenances can lead to strongly differing behaviour. Therefore, the authors want to show the usability of atmospheric air conditioning as realistic LTA procedures using different temperatures. Furthermore, a new ageing / conditioning method N-VAPro was developed to isolate non-oxidative LTA effects from oxidative LTA effects using nitrogen storage on mix level. The following conclusions can be summarised.
• Considering realistic field conditions (max. +65°C on the asphalt surface), non-oxidative effects should not be triggered by laboratory LTA procedures since they are not expected to occur in the field.
• To prevent unrealistic non-oxidative ageing effects, conditioning temperatures must kept below 110°C.
• To achieve a long-term ageing stage, ageing durations higher than 4 days are necessary when using atmospheric air ageing at realistic ageing temperatures for HMA samples.
• Using two similar bitumen sources (same grade, different provenances) for HMA can result in a differing ageing behaviour.

Below a certain temperature threshold for LTA methods of HMA, the conditioning hardly triggers any oxidative effects in a short amount of time and is therefore inefficient. Additionally, at temperatures above +130°C, the viscosity of some binder grades is so low that permanent changes in the structure of compacted HMA specimens are likely to appear upon conditioning for an extended period. The results from mechanical tests of such samples are therefore biased.

Summarising, to achieve both, realistic and efficient LTA procedures for HMA, temperature have to stay well below +110°C and oxidative ageing effects have to be increased by other means, e.g. ageing time or the use of more reactive gases that are present in the atmosphere as well.

It must not be overlooked that ageing on HMA level can lead to different results than ageing the same bitumen on the binder level. Taking into account that the PG grade of binder II has a wider range and PG grading considers the aged behaviour of binder, ageing these binders at asphalt levels leads to different results. Furthermore, binder II was only aged for 3 days on HMA level (binder I: 4 days). Nevertheless, similar ageing results were achieved. In this case, only plain binder without polymer modifications or any mix additives (e.g. waxes, rejuvenators, RAP) were used. These modifications carried out on the HMA level can only be assessed partially after binder recovering since not all additives end up in the recovered binder. Thus, ageing of compacted HMA specimens is necessary. It is particularly interesting that the hypothesis of ageing starting points for binders can be seen within this project. This has to be analysed for more binders. Furthermore, a double exponential increase with ageing temperature on the binder level was shown.

5.2. Outlook

This paper is limited to the binder used for the development of the method. A study of the ageing behaviour on HMA and binder level with binder from different sources should give a better idea of ageing in general. Therefore, a combination of oxidative ageing methods (e.g. VAPro, oven ageing of loose mixture) and non-oxidative ageing methods (e.g. N-VAPro) at realistic temperatures (e.g. +60–95°C) can give a comprehensive insight.

Even stronger dependencies on the ageing temperature appear by the use of additives (e.g. polymers, waxes, rubber). Many of these products can change the viscosity non-evenly across the performance temperature range or at production temperatures. For these additives, a combination of the presented methods can give a broader and more realistic perspective about the feasibility.

Disclosure statement

No potential conflict of interest was reported by the authors.
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