Comparative characterization of aged bitumen properties

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Abstract. To provide higher rates of reclaimed bitumen uses in road industry better understanding about aging of bitumen is needed, which requires to get complete information about influence of aggressive environmental factors on bitumen. In this paper changes of bitumen structural and rheological parameters upon ageing are evaluated by using one of the most known method, RTFOT in comparison to alternative procedures, as thermal and ultraviolet light irradiation induced aging. Calorimetric properties of the raw and aged bitumens are determined by MDSC, chemical composition by FTIR and rheological parameters (viscosity, rutting resistance and fatigue cracking resistance) by DSR. The results confirm that mentioned alternative aging procedures can be used to some extent for prediction of real field-aged bitumen properties changes.

1. Introduction
Asphalts pavement service life depends on several environmental factors, including traffic load, climate and temperature, but the main factor is used binder. Most frequently used binder is bitumen; it is viscoelastic and waterproofing material derived from crude oil. As organic material bitumen, ages faster than others asphalt components. With bitumen aging generally oxidation is understood, but it also includes evaporation of volatile components, consequently, chemical structure is changed which affects other important service life properties, such as, rheological behavior. Aged bituminous materials are harder, more brittle and are characterized with higher viscosity, which reduces adhesion between pavement components [1,2].

The study of bitumen rheology and structural properties after aging is not a new field, over the years several methods have been developed for prediction of aging process in laboratory conditions, because uses of reclaimed asphalt increases [3].

Main methods for prediction of bitumen aging are rolling thin film oven test (RTFOT) and pressurized aging vessel (PAV) test for prediction of short-term and long term aging, respectively, but these methods do not include influence of ultraviolet light (UV) irradiation on the bitumen. The aim of this study is to evaluate bitumen properties after several aging procedures, including UV irradiation, and evaluate the effectiveness of the used aging methods [1,2].

2. Materials and methods
Commercial 70/100 penetration grade bitumen was used. Properties of the bitumens after different aging procedures were assessed: reclaimed asphalt pavement (RAP) derived bitumen; RTFOT aged bitumen as accords to ASTM D2872; thermally aged bitumen (70/100: 8T), obtained by
mixing of bitumen at 185-188 °C for 8 hours, and UV aged bitumen (70/100:UV167 and 70/100:UV330), obtained by using QUV accelerated weathering tester utilizing UV-A 340 nm lamps with irradiance of 0.89 W/m² for different duration times (167 and 330 hours) at 60 °C.

Infra-red spectra were recorded by using Fourier transform infrared spectrometer Thermo Fisher Scientific, Nicolet 6700 in attenuated total reflection (FTIR-ATR) mode in the range of wave numbers from 4000 cm⁻¹ to 650 cm⁻¹.

Calorimetric properties were measured by using differential scanning calorimeter DSC-3 (Mettler Toledo) utilizing modulated technique TOPEM (MDSC). Average sample mass was ca 10 mg. Test regime: heating from -90 °C to 60 °C with heating rate of 1 °C/min.

Rheological behaviour of unaged bitumen and aged bitumen was characterized by using RELOGICA StressTech NOVA rotational viscometer NOVA (DSR) by utilizing 25 mm plate-and-plate configuration to carry out oscillatory shear tests at various temperatures (46, 58, 70, 82 °C).

3. Experimental part

Bitumen aging is very complex process, involving variety of reactions, thus making interpretation of data challenging. Consequently, MDSC analysis has been performed to determine influence of aging process on the amorphous and crystalline phases of the bitumen constituents, as it is known that heat flow in MDSC can be separated into reversing and non-reversing components, respectively attributable to the processes that can be brought to equilibrium and those, controlled by kinetics. In Figure 1 reversing and non-reversing heat flow curves of the bitumen samples are shown. Fig. 1 (a) shows very broad range of overlapping structural relaxations/glass transitions Tg for all samples over the temperature diapason of -90 – 0 °C. Besides it, inexpressive endothermic peaks (e.g. for 70/100:8T around 10 °C), most probably attributable to melting of semi-crystalline constituents, can be also observed, evidently, due to the fact that melting of crystals at certain experimental conditions can contain also some reversing contribution. Non-reversing heat-flow curves, depicted in Fig. 1 (b), give more detailed information about the effects that cannot be brought to equilibrium, for instance, evaporation, oxidation, decomposition, and at certain experimental conditions crystallization. Thus, endothermic peaks, observed starting from ca -10 °C can be attributed to crystallization of the saturate fractions in bitumen [4]. Plausible, due to ageing these endothermic contributions are increased, resulting in increased crystallinity of bitumen, aged by different procedures. It should, however, be mentioned that isotropization of fractions other than the saturates should be also regarded as contributors to the observed endotherms [4].

The derivative of heat capacity temperature relationships \( C_p' \)-T allows improved analysis of relaxation processes. From previous results, we observed broad relaxation region, but in Figure 2, multiple peaks within this region are distinguishable. Masson et.al. [4, 5] have concluded, that bitumen
is characterized with four T_g that arise from different phases in bitumen, as it is known that bitumen has complex chemical composition, consisting from saturates (S), aromatics (A), resins (R) and asphaltenes (A), which ratios strongly depend on the refinement process of the crude oil [1,2]. It is generally known that decrease in aromatics content and an increase in resins and asphaltene fractions occurs upon ageing, resulting in the change of the ratio between the SARA fractions. However, these effects are hardly recognizable due to “noisy” nature of the derivative curves.

![Figure 2. 1st derivative of Cp_v^-T relationships of unaged and aged bitumen](image)

The change in chemical composition, including SARA fractions, of bitumen under aging can be also determined by FTIR analysis, because at oxidation ketones, dicarboxylic anhydrides, carboxylic acids and sulfoxides are formed, as characterized by appearance of carbonyl (C=O at 1705 cm\(^{-1}\)) and sulfoxide (S=O at 1030 cm\(^{-1}\)) groups. This method is often used for characterization of ageing process of asphalt pavement binder.

![Figure 3. FTIR spectra of unaged and aged bitumens in carbonyl group (a) and sulphoxide group (b) absorption regions](image)

In Figure 3 and Table 1 it is observed, that sulfoxide peaks intensities as well as respective sulfoxide indices of neat and aged bitumens are higher in comparison to those, characterizing carbonyl
groups. According to literature S=O groups form faster than C=O groups, furthermore, the former can be present even before aging, while it depends from the used crude oil [6,7]. Carbonyl (Ico) or sulfoxide (Iso) indexes are calculated according to equations (1-2):

\[
\begin{align*}
I_{co} &= \frac{I_{1700}}{I_{\text{reference}}} \\
I_{so} &= \frac{I_{1030}}{I_{\text{reference}}}
\end{align*}
\]

where \(I_{1700}\) is the amplitude of carbonyl group centred at 1700 cm\(^{-1}\), \(I_{1030}\) is the amplitude of sulfoxide group centred at 1030 cm\(^{-1}\) and \(I_{\text{reference}}\) is the amplitude of ethylene and methylene groups which are considered not to be significantly affected by aging process (1460 and 1375 cm\(^{-1}\), respectively) [6].

| Table 1. Ico and Iso of unaged and aged bitumens |
|-----------------|-----------------|
| Iso  | Ico  |
|---|---|
| 70/100  | 0.12 | 0.02 |
| RAP     | 0.38 | 0.11 |
| RTFOT   | 0.18 | 0.04 |
| 70/100:8T | 0.18 | 0.04 |
| 70/100:167UV | 0.26 | 0.14 |
| 70/100:330UV | 0.33 | 0.14 |

Increase in the intensities at the absorption region of C=O and S=O groups is expected after all aging procedures. By increasing UV irradiation exposure time one can clearly see that at higher exposure times greater intensities at C=O and S=O groups absorption regions are observed, sulfoxide index almost reaches the value, characteristic for RAP. Concomitant, the values of Ico of the UV aged bitumens are higher in comparison to that of RAP derived bitumen regardless of UV irradiation exposure time.

Influence of oxidized groups on the bitumen stiffness can be various, it depends of dispersing power of non-associating components and strength of the polar molecules [7]. In our investigation it is observed, that viscosity of the bitumen derived from RAP at 46 °C is higher (above 800%) than that for unaged bitumen (see Fig.4 (a)). Viscosities of the bitumens, aged by other procedures, don’t increase so drastically, values are between unaged bitumen and RAP derived bitumen. At higher temperatures viscosity values of the investigated bitumens decrease, but keep before observed relationship.

Rheological behaviour is also characterized with rutting resistance parameter \((G*/\sin\delta)\) and fatigue cracking resistance parameter \(G*\sin(\delta)\). Plots of \(G*/\sin\delta\) versus temperature are displayed in Figure 4 (b). As already expected, critical temperature of the investigated materials is higher for aged bitumens, especially RAP derived bitumen, it is considerably stiffer than 70/100 or any other of the aged bitumens.
Values of fatigue cracking resistance parameter $G^* \sin(\delta)$ of the investigated bitumens are summarized in Figure 5. Bitumen is more elastic, if the parameter is lower. According to AASHTO T 315 for bituminous materials to resist fatigue cracks, $G^* \sin(\delta)$ for RTFOT+PAV-aged bitumen should not be greater than 5000 kPa. By applying this value to the investigated aged bitumens one can see that RAP has the lowest critical temperature in comparison to any other aged bitumen.

**Figure 5.** Fatigue cracking resistance parameter $G^* \sin\delta$ of unaged and aged bitumens.

**Conclusions**

Results of the study show that under the influence of temperature and UV irradiation the investigated bituminous materials undergo aging, which is similar to some extent with the field aging of bitumen. Because of aging chemical structure of bitumen is affected, i.e., bitumen becomes more polar as confirmed by increasing intensities in the carbonyl (C=O) and sulfoxide (S=O) groups absorption regions. Aging of bitumen causes also increment in endothermic contributions of non-reversing heat flow curves, which could be related to increased crystallinity. Due to the changes in the investigated bitumens chemical composition, including SARA fractions, it viscosity values are increased, rutting resistance parameters increase and fatigue cracking resistance parameter increases.

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