

**Aging effect on rheology and cracking behaviour of reclaimed binder with bio-based rejuvenators**

Authors: Cavalli M. C. <sup>a, b\*</sup>, Zaumanis M. <sup>a</sup>, Mazza E. <sup>a, b</sup>, Partl M. N. <sup>a</sup>, Poulidakos L. D. <sup>a</sup>

<sup>a</sup> Empa, 8600 Dübendorf, Switzerland

<sup>b</sup> ETH Zurich, Institute for Mechanical Systems, 8092 Zürich, Switzerland

\* Corresponding author

Überlandstr. 129, 8600 Dübendorf

+41 58 765 4807

MariaChiara.Cavalli@empa.ch

This document is the accepted manuscript version of the following article:  
Cavalli, M. C., Zaumanis, M., Mazza, E., Partl, M. N., & Poulidakos, L. D. (2018). Aging effect on rheology and cracking behaviour of reclaimed binder with bio-based rejuvenators. *Journal of Cleaner Production*, 189, 88-97. <https://doi.org/10.1016/j.jclepro.2018.03.305>

This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

**Abstract**

Reclaimed asphalt pavement (RAP) is stiffer than the virgin material due to aging, thus it is expected to have worse cracking resistance. By adding bio-based rejuvenators, RAP binder mechanical performances at low temperatures improve: fracture toughness temperature of RAP decreases after the addition of rejuvenators to a level similar to the virgin binder. Furthermore, work to fracture of RAP binder increases after the addition of rejuvenators. Addition of rejuvenators to RAP binder can restore both mechanical properties and toughness at low temperature. However, despite the rejuvenators' addition, physio-chemical oxidation did not reverse as mechanical changes were not caused by chemical changes at functional groups level. Results confirmed how considering the effect of aging is crucial when studying how rejuvenators affect the RAP binder chemically and mechanically.

**Keywords:** reclaimed asphalt; rejuvenators; cracking resistance; rheology; oxidation

## 1. Introduction

Due to exposure to cold temperatures, asphalt binders shift from time dependent ductile to brittle behaviour, increasing the risk of crack formation (Baek et al., 2011; Li et al., 2008). This is even more detrimental with reclaimed asphalt pavement (RAP) materials which contain aged and stiffer RAP binder (the binder around RAP's aggregates) which has potentially higher susceptibility to crack formation than virgin binders (Cavalli et al., 2017). In order to reduce its brittleness, viscosity and stiffness RAP binder are modified by adding so-called "rejuvenators" which are generally obtained from natural resources (Dedene and You, 1997; Mangiafico et al., 2015; Zhu et al., 2017). The effectiveness of rejuvenators is usually measured by comparing standard engineered tests such as the penetration and softening point of the rejuvenator-aged bitumen blend with reference values of the virgin binder. However, by correlating rheological and microstructural techniques, the mechanism and performance of rejuvenation can be understood. For instance, the addition of the bio-based oil as recycling agent was observed to generally lower the complex moduli and improve fatigue performances of mixtures with a RAP content equal or greater than 40% (Mangiafico et al., 2015). In another study, vegetable based oil and maltene base rejuvenators provide similar flow property improvement for highly aged binders (Huang et al., 2015). Recently, different types of organic oils have been tested as recycling agents to restore the viscosity and elasticity of aged asphalt (Zhang et al., 2017). For instance, recycled cooking oil is a good candidate for improving the low-temperature grade (Qurashi and Swamy, 2018; Raman et al., 2015; Sun et al., 2017). In another research, polyethylene terephthalate (PET) derived products have been seen as a performance-enhancing additive for asphalt (Leng et al., 2018). Time-temperature behaviour and possible mechanical restoration achieved by rejuvenators may be determined with the dynamic shear rheometer (Ali et al., 2016) whereas resistance to failure at low temperature may be characterized by fracture toughness, derived from the energy causing fracture (Anderson et al., 2001; Kang et al., 2017; Ritchie, 2011). Since RAP binder is aged and brittle, it is susceptible to cracking especially at low temperatures. Therefore, low temperature performances is an important property to be investigated when utilizing reclaimed asphalt (Hoon Moon et al., 2017). Strong cracking resistance is desirable in road engineering especially for cold temperature countries as the material is able to remain more viscous at lower temperature (Bueno et al., 2015). However, systematic approaches are missing to understand the effect of rejuvenators in restoring the properties of RAP binder and how the RAP binder with rejuvenator is affected by aging. This then demonstrates the necessity to investigate the aging process in RAP and virgin binders and also the role of rejuvenators in the binder oxidation.

In this work, a fracture toughness test (FTT) is used as a possible alternative to traditional test method such as for example bending beam rheometer (BBR), for determining low temperature properties and crack susceptibility of modified RAP binders with rejuvenators. The analysis of covalent bonds due to the aging process can be successfully done with Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR). The combination of FTIR-ATR and rheological

measurements can show how aging is a fundamental parameter when considering the effectiveness of rejuvenators.

The objective of this work is to evaluate the low temperature cracking as well as rheological behaviour of RAP binder modified with bio-based rejuvenators at aged and unaged state. In addition, oxidation caused by aging and the effects of rejuvenators on RAP binder at functional groups level is analysed. A summary table of all the tests presented in this paper can be found below.

Table 1 Summary table of all the tests presented.

Test	Aim
Fracture toughness	Low temperature cracking behaviour
Dynamic shear rheometer	Time-temperature behaviour
Attenuated total reflectance-Fourier transform infrared spectroscopy	Changes at functional groups level

## 2. Materials and methods

RAP binder from a Swiss provider was extracted and recovered from a RAP mixture (EN 12697-1). The binder content from RAP was found to be 5.6% by weight of the mixture with a needle penetration of  $22 \times 10^{-1}$  mm at 25° C (EN 1426) and a softening point temperature equal to 65.7° C (EN 1427). A virgin penetration graded bitumen 50/70 with a measured penetration of  $62 \times 10^{-1}$  mm at 25° C and a softening point temperature of 49° C was used as reference. The reason for this choice was that this investigation is part of a larger study including virgin mixture evaluation which has a 50/70 penetration binder. Three commercial bio-based rejuvenators were used: rejuvenator “A” based on seed oil rejuvenator “B” based on cashew nut shell oil and rejuvenator “C” based on tall oil. The rejuvenator’s dosage was set to be 5% by mass of the recovered RAP binder as by adding 5% of each rejuvenator the RAP binder reached a penetration between  $50 \times 10^{-1}$  mm and  $70 \times 10^{-1}$  mm as was the target penetration of virgin binder. Penetration was chosen as reference test for various reasons. Primarily, this test is well known worldwide and could be duplicate easily. The rejuvenator’s dosage calculation with penetration would provide a practical tool to select the initial dose before conducting any other tests and it would allow adjusting the recycling agent dose to account for slight changes in RAP binder penetration. In addition, many researches have shown the effectiveness of penetration as starting point to add the exact quantity of rejuvenator in the RAP binder (Ji et al., 2017; Ongel and Hugener, 2015; Zaumanis et al., 2014).

The extracted RAP binder was placed in the oven at a temperature equal to 110° C for 20 minutes. This temperature allowed the binder to become soft and workable but at this low temperature and exposure time the binder is not expected to age significantly. This amount of time and temperature were found to be the minimum necessary for 100 g of RAP binder to become liquid; further exposure to temperature was avoided to reduce excessive aging. Afterwards, rejuvenators, which were at room temperature, and the hot RAP binder were mixed in a speed mixer for one minute at 3500 rounds per minute, this resulted in a homogeneous mixture that was verified by the unaided eye. All binder materials were also tested after laboratory aging. Samples were aged first using the rolling thin-film oven test (RTFOT) which aims at simulating aging during mixing and paving (EN 12607-1). The samples were placed into rolling glass jars at 163° C for 85 minutes while undergoing oxidation by airflow of 400 mL/min. After the RTFOT, the samples were further conditioned with the pressure aging vessel (PAV) method (14769:2012) that uses pressure of 2.10 MPa for 20 hours at 100° C. The combined aging procedures are expected to simulate mixing, laying and field aging of virgin asphalt binders at later stages of pavement life (Mousavi et al., 2016; Yang et al., 2017).

The table below summarizes all the materials used in this research.

Table 2 Summary table of all materials tested in this study.

Material Type	Designation before aging	Designation after aging (RTFOT + PAV)
Virgin binder	50/70	50/70 aged
Reclaimed asphalt binder	RAP	RAP aged
Reclaimed asphalt binder + 5% seed oil	RAP + 5% A	RAP + 5% A aged
Reclaimed asphalt binder + 5% cashew nut shell oil	RAP + 5% B	RAP + 5% B aged
Reclaimed asphalt binder + 5% tall oil	RAP + 5% C	RAP + 5% C aged

## 2.1 Fracture toughness test

The fracture toughness test (FTT) is based on a European standard (European Committee for Standardization CEN TS15963, 2010). As shown schematically in Figure 2, it is a three-point bending test where the sample presents a thin notch in the middle. The samples are tested in a temperature controlled bath to cool the sample from room temperature down to the one desired for testing (range - 10° C/0° C). The liquid used is 99.5% ethanol. The use of ethanol as cooling fluid has been studied previously and it was considered having less influence on bitumen's surface characteristics as compared to other cooling media such as potassium acetate (Cannone Falchetto et al., 2012). Samples were prepared by heating 12.5 g of all binders at 110° C for 10 minutes to ensure the required

viscosity for pouring the material in metal moulds without significant aging. For each binder type, pre-notched samples were created. As shown in Figure 1, the pre-notch of 5 mm depth was introduced by inserting a 0.15 mm double film polyvinyl chloride paper in the middle of the specimen. As depicted in Figure 1, to avoid sticking between samples, the binder's moulds were separated by a transparent film (0.125 mm) smeared with a small amount of synthetic grease.

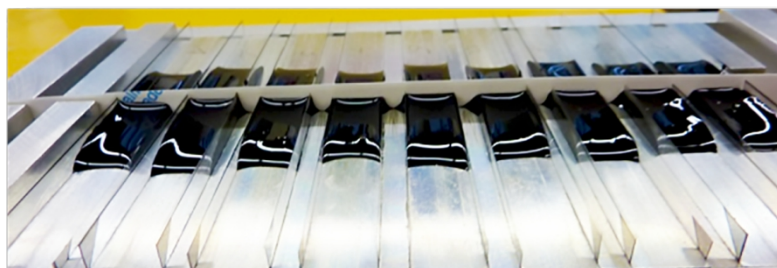


Figure 1 FTT moulds with paper to impose a pre-notch.

The specimens were then left for one hour in the ethanol cooling bath prior to testing. Subsequently, a vertical load was applied with a constant displacement rate of 0.01 mm/s until failure of the specimen.

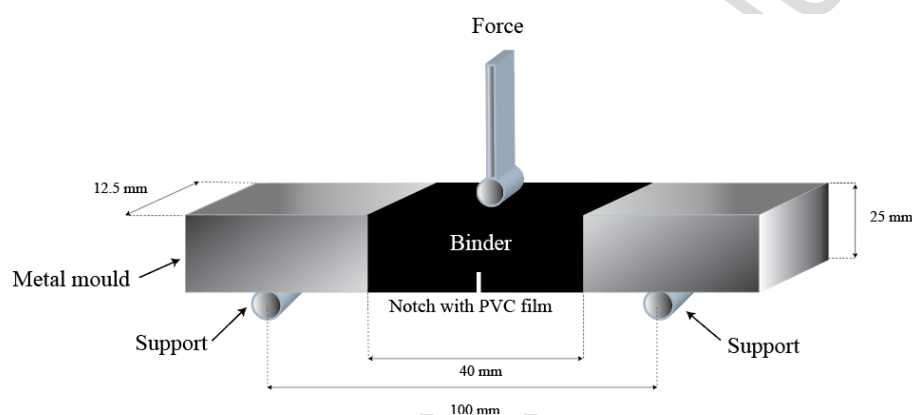


Figure 2 Schema of the fracture toughness test setup.

The fracture toughness temperature ( $T_{FTT}$ ) of a bituminous binder is defined in the standard (CEN/TS 15963:20) as the temperature at which the deflection in the middle span at maximum force is equal to 0.3 mm. In order to calculate such temperature, the fracture toughness test was repeated at different temperatures until a deflection  $\geq 0.3$  mm was measured. As Figure 3 demonstrates, the interpolated line between  $T_1$  and  $T_3$  was calculated. Afterwards, for each temperature the force vs. deflection curve was measured. In this case  $T_2$  is satisfying this criterion but not  $T_1$  and  $T_3$ , thus,  $T_2$  corresponds to the fracture toughness temperature.

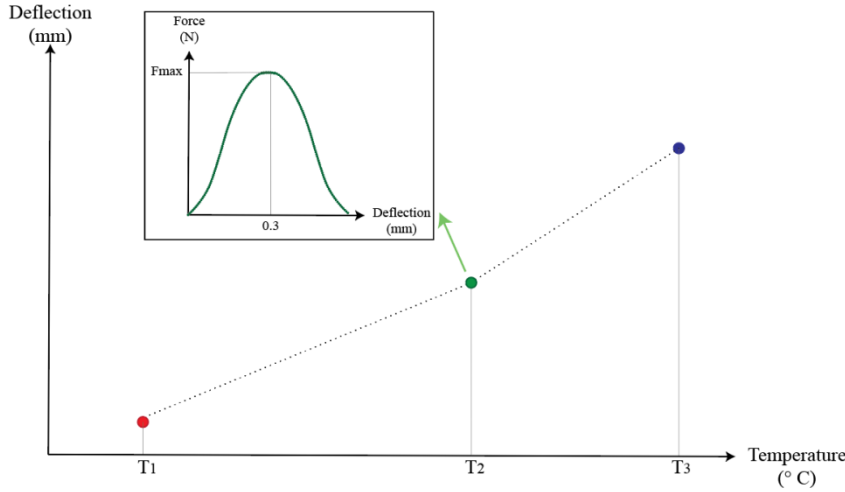


Figure 3 Temperature vs deflection plot and the corresponding force-deflection curve for temperature  $T_2$  (satisfying the FTT requirement of 0.3 mm).

## 2.2 Dynamic shear rheometer

Rheological properties of the binder can be expressed in terms of its complex shear modulus  $G^*$  which is composed of two frequency and temperature dependent components  $G'$  and  $G''$ , representing the dynamic storage and loss moduli respectively. Those values are generally measured through sinusoidal loading in a dynamic shear rheometer (DSR). With the phase angle  $\delta$  between sinusoidal input and the viscoelastic material response follows

$$G^* = |G^*|(\cos \delta + i \sin \delta) = G' + i G'' \quad (1)$$

$$|G^*| = \sqrt{(G')^2 + (G'')^2} \quad (2)$$

$$\delta = \tan^{-1} \frac{G''}{G'} \quad (3)$$

$G'$  gives an indication of the ability of the material to store energy while  $G''$  gives an indication of the energy loss. In this work, the sigmoidal model proposed by Witczak (Witczak and Fonseca, 1996) was used for modelling  $|G^*|$  with equation:

$$\log |G^*(\xi, T)| = \log |G_l^*| + \frac{D}{1 + e^{\frac{A - B(\log f + \log a_T)}{D}}} \quad (4)$$

The stiffness modulus depends on the reduced frequency,  $\xi$ , and temperature  $T$ , and the following four parameters:  $\log |G_l^*|$  is the lower asymptote of the sigmoidal curve,  $D$  is the difference between the upper and lower asymptote,  $f$  is the cyclic frequency and  $A$  and  $B$  are defined as shape coefficients. In this study, the shift factor  $a_T$  was calculated with the Williams-Landel-Ferry relation (Williams et al., 1955):

$$\log a_T = \frac{-C_1(T - T_{ref})}{C_2 + (T - T_{ref})} \quad (5)$$

where  $C_1$  and  $C_2$  are material related constants. The reference temperature  $T_{ref}$  in this study was 20° C. In order to achieve the best fit between the measured values and the values from the sigmoidal model, the algorithm proposed by Gergesova (Gergesova et al., 2011) was used.

Following the procedure in the EN 14770, 1.5 g of each material was placed in a disc shaped silicon mould with a diameter of 8 mm and tested with the DSR Physica MCR at temperatures between -10° C to +40° C. A 25 mm mould was used for measuring from +50° C to +80° C. Each measurement was repeated four times and averaged values were displayed for frequencies between 0.1 to 20 Hz at each temperature. The chosen frequencies were expected to simulate traffic vehicles passing during service life (Airey et al., 2004).

### 2.3 Attenuated total reflectance Fourier transform infrared spectroscopy

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) is a technique for determining chemical functional groups within a medium and it was used to characterize chemical changes due to aging and addition of rejuvenators in the material. ATR-FTIR measurements were performed following a previous set-up as outlined in (Cavalli et al., 2018). In the case of aging in bitumen, such as in RAP binder, it is well established that changes in the intensity of the spectral peaks corresponding to carbonyl (peak around 1700cm<sup>-1</sup>) and sulfoxide functional groups (peak around 1030cm<sup>-1</sup>) are relevant as reported in (Petersen and Glaser, 2011). The ATR-FTIR measurements were performed at room temperature in a Tensor 27 from Bruker spectrometer using a diamond crystal. For the spectroscopy measurements, a small amount of bitumen (ca.10 mg) was placed directly on the diamond crystal with a metal spatula. The spectra were collected in the 4000 to 500 cm<sup>-1</sup> wavenumber range with a resolution of 4 cm<sup>-1</sup> and each spectrum represented an accumulation of 32 spectra.

## 3. Results and Discussion

### 3.1 Attenuated total reflectance-Fourier transform infrared spectroscopy

#### 3.1.1 RAP and virgin binder

Any organic material evolves with time, due to aging. This is also true for bituminous materials which are submitted to two main aging mechanisms: during fabrication, the mixing process with aggregates at high temperature and during the laying process on the road and subsequently, during the service life in the pavement where their evolution is slower but steady. Asphalt is made up largely of hydrocarbons, together with other molecules or molecular structures. These molecules generally consist of groups of carbon, hydrogen, sulphur, oxygen and nitrogen, as well as a little amount of

metals (Lamontagne et al., 2001). Chemical functional groups are groups of atoms which are responsible for different reactions within a compound.

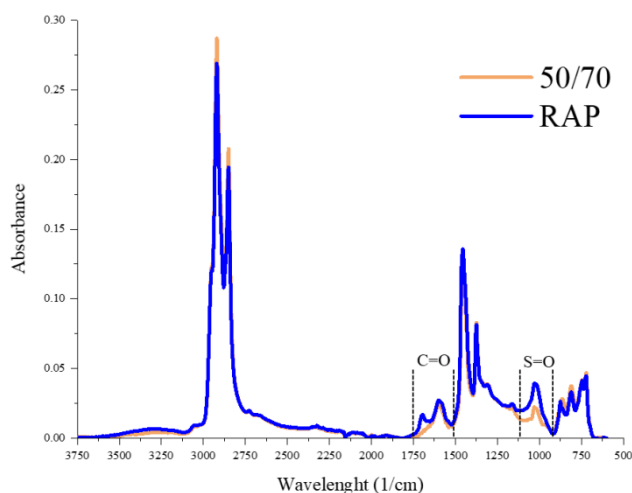


Figure 4 ATR-FTIR spectra of the virgin binder 50/70 and the RAP binder.

As in Figure 4, by comparing 50/70 virgin binder and RAP binder, several peaks can be identified in both spectra. The sulfoxide group, corresponding to a band location between 1060  $\text{cm}^{-1}$  and 1030  $\text{cm}^{-1}$ , and the carbonyl group (peak centred around 1700  $\text{cm}^{-1}$ ) showed higher absorbance for the RAP binder. This is an indication of how the RAP binder, since it is already aged, presents higher peaks intensity due to aging at functional group level.

### 3.1.2 Rejuvenators composition

Additional analyses were done to detect differences in the rejuvenators without the addition of any bitumen. Rejuvenators A and C have shown to be chemically similar while B showed significant differences as shown in Figure 5.

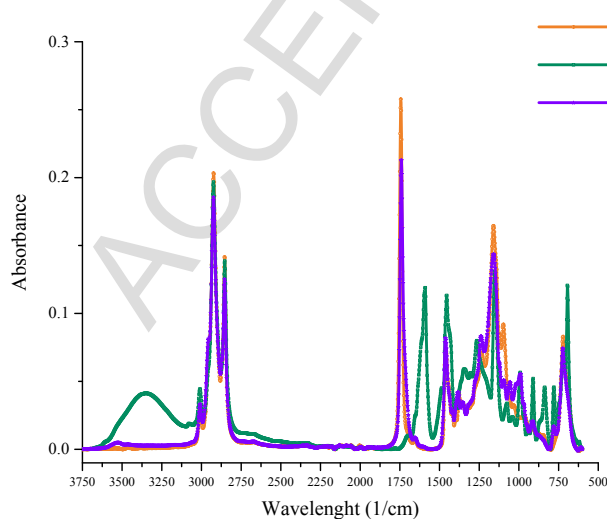


Figure 5 ATR-FTIR spectra of rejuvenator A, rejuvenator B and rejuvenator C.

As already mentioned, rejuvenator A is a seed oil, mainly composed of palmitic acid (saturated usually 5%), stearic acid (6% saturated), oleic acid (30% monounsaturated omega-9) and linoleic acid (59% polyunsaturated omega-6) (Karen et al., 2016). Tall oil fatty acids (TOFA) are usually used for bio-based thermosets. The tall oil itself cannot be used as a matrix in composite materials, because the carbon-carbon double bonds inside the material, are not sufficient enough to start polymerization to give resins any degree of stiffness or structural strength. However, active functional groups can be introduced artificially. Rejuvenator B is a cashew nut shell oil (CNSL) which is a by-product of the cashew industry: the nut has a shell inside which is a soft honey comb structure containing a dark reddish brown viscous liquid. It is a very well-known industrial product which has innumerable applications, such as rubber for surface coatings. The liquid phase extracted from CNSL is mostly composed of anacardic acids (70%), cardol (18%) and cardanol (5%) (Menon et al., 1985). As in Figure 5, rejuvenator B can contain the hydroxyl group.

In order to study any degradation due to oxidation, rejuvenators alone were placed in an oven for 3 hours at 160° C. This procedure was conceived to detect any variations in the chemical compositions due to overheating. The oven temperature and the amount of time were considered consistent with the maximum amount of time used in the mixing procedure, as in the European Standard EN 12697. As mentioned in (Cavalli et al., 2018), results indicated that no changes to the chemical bonds/functional groups were recorded and therefore the three rejuvenators by themselves appear not to change significantly their chemical compositions after the heating process.

### 3.1.3 *RAP plus rejuvenators*

As it is possible to see from Figure 6, the sulfoxide group and the carbonyl group, do not disappear even when rejuvenator was added to the RAP binder. Furthermore, chemical structures of RAP + 5% C and RAP + 5% A were found to be similar, suggesting that rejuvenator C and rejuvenator A can have similar effect on the RAP binder from the chemical point of view. For example, a peak corresponding to a wavelength of 1745 cm<sup>-1</sup> and corresponding to the -C=O- ester group was found.

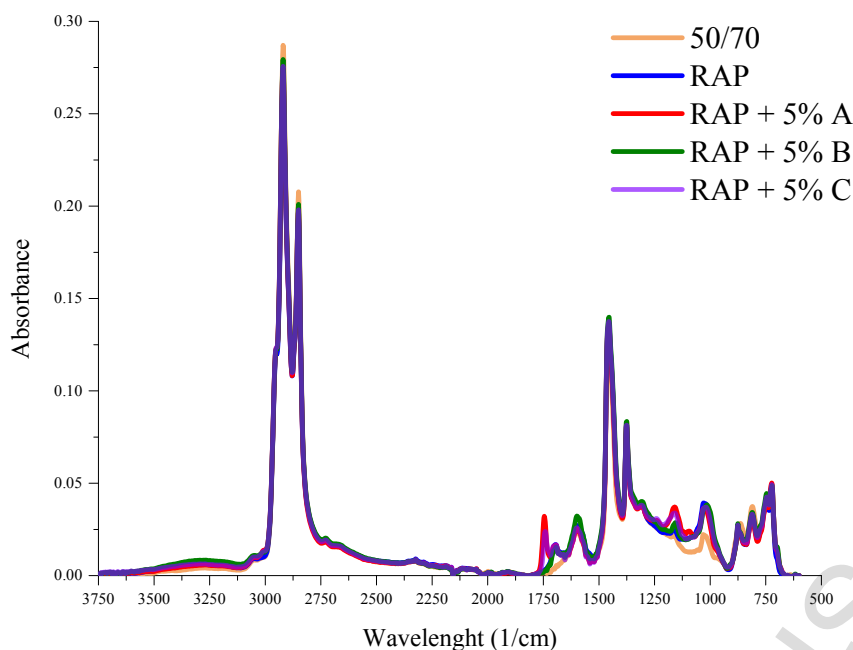


Figure 6 ATR-FTIR spectra of the virgin binder 50/70, the RAP binder and the RAP binder added with rejuvenator A, B and C.

The presence of higher carbonyl and sulfoxide groups in all RAP binders compared to the virgin binder, implies rising degree of oxidation (Mousavi et al., 2016; Petersen and Glaser, 2011). As shown in Figure 6, RAP + 5% A and RAP + 5% C produced a higher absorbance in the spectra at wavenumber corresponding to the carbonyl index than the plain RAP binder. This may be due to the fact that seed oil and tall oil themselves contain carboxylic groups  $C=O$ , as outlined in (Jia et al., 2014). In conclusion, it can be observed how the addition of rejuvenators could soften the RAP binder. Despite that, rejuvenators were not able to break functional groups caused by oxidation as demonstrated in (Cavalli et al., 2018). As shown in the previous sections, rejuvenator alone were not affected by aging thus, the increase of both  $C=O$  and  $S=O$  groups is a result of aging of the RAP binder as shown in previous researches as well (Dondi et al., 2016; Lopes et al., 2016)

### 3.2 Fracture toughness

Force-displacement curves at  $-10^{\circ}C$  are shown in Figure 7 where relative standard deviation of four repetitions can be seen. In general, as expected lower force compared to other samples was needed to cause cracking in the RAP binder. Virgin binder 50/70 showed a force equal to  $8 \pm 1$  N before cracking. By adding rejuvenators in the RAP binder, a higher force was necessary to start cracking compared to the RAP binder. Both RAP + 5% B and RAP + 5% C showed a force close to  $9 \pm 1$  N while RAP + 5% A needed a force of  $11 \pm 0.5$  N before crack initiation. Thus, after adding the rejuvenator, the maximum cracking force increased between 30% and 50% compared to the RAP

binder, depending on the rejuvenator. As expected, after aging, the value of the maximum cracking force decreased (Figure 7 right). This indicates that the material becomes more brittle thus, being more susceptible to low temperature cracking. By comparing all curves, it can be observed how aging has a significant effect for all the binders. After aging, all the curves shifted to the left towards lower deflection indicating less ductility compared to unaged stage.

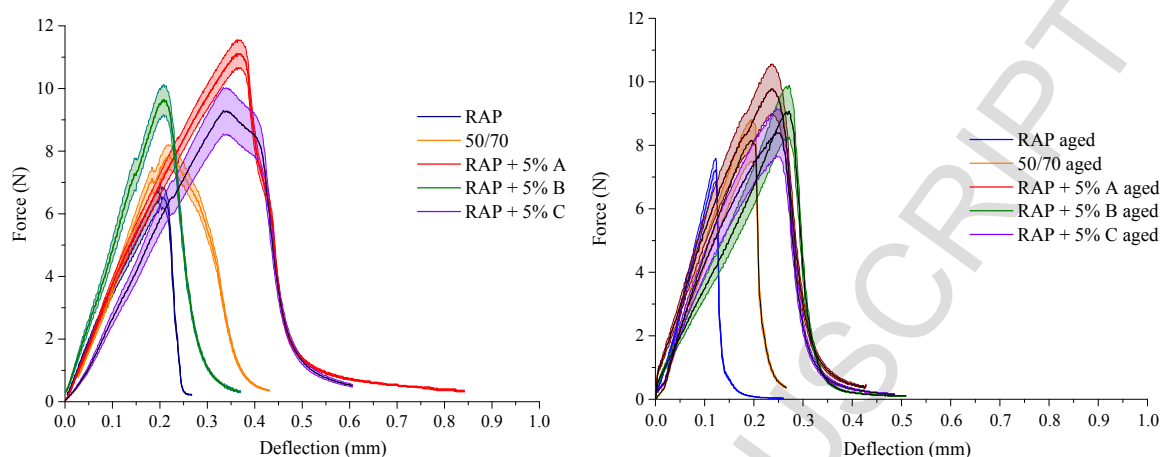


Figure 7 Force vs deflection curves for all the unaged (left) and aged (right) binders at  $-10^{\circ}\text{C}$ . The standard deviation for each point was calculated as average of four measurements.

In order to assess low temperature behaviour resistant of binders, a performance index is introduced. The work to fracture, as depicted in Figure 8, can be calculated from the force-displacement curve. This index can provide indication of the cracking resistance of the binders.

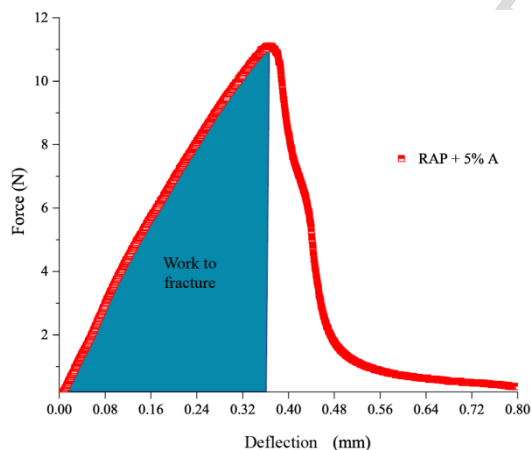


Figure 8 Example of the area representing the work to fracture.

As can be seen in Figure 9, after aging all the binders tested decreased their work to fracture, thus becoming more susceptible to low temperature cracking before the unaged state. These results demonstrate how aging has a significant effect on low temperature cracking behaviour. In addition, RAP binder performance at low temperature at both aged and unaged state show significant improvement after adding the rejuvenators. In particular, at unaged state, RAP + 5% A and RAP + 5% C could increase the RAP binders work of fracture up to 50% and RAP + 5% B up to about 40%.

Furthermore, at low temperature ( $-10^{\circ}\text{C}$ ), RAP binder appeared more sensitive to aging than the virgin binder, halving its work to fracture. The work of fracture decreased for all modified binders, although it remained higher than virgin and RAP binder. The results confirm that, despite the aging procedure, rejuvenator could improve the crack resistance of RAP binder at  $-10^{\circ}\text{C}$ . Besides, the type of rejuvenator had a significant effect on fracture behaviour of RAP binder. Even after aging, all rejuvenated binders showed higher work to fracture than virgin binder, as shown in Figure 6. Moreover, it can be observed how the extracted RAP binder alone decreased its work to fracture after aging. Virgin binder does not show such a trend in fact, its variation after aging is negligible. This can indicate how, although the RAP is already aged, it tends to age more compared to the virgin binder at low temperature conditions.

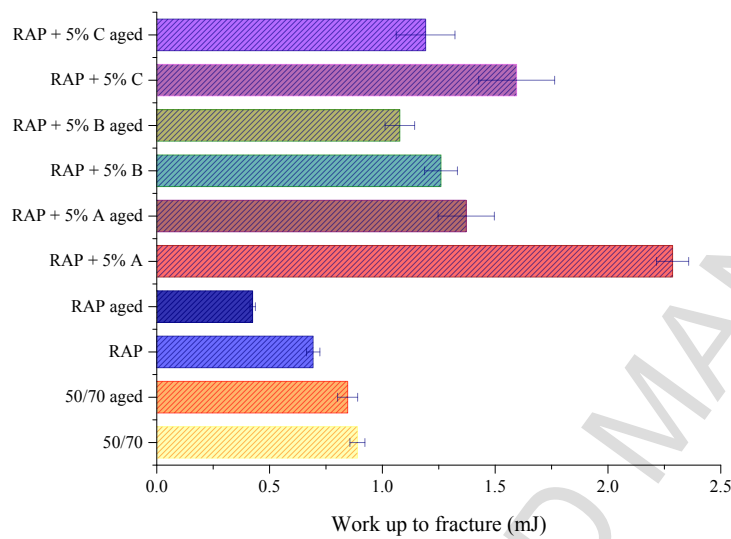


Figure 9 Work of fracture at crack initiation at  $-10^{\circ}\text{C}$  before and after aging. Standard deviation was obtained as average of four measurements.

### 3.2.1 Fracture toughness temperature

To obtain a comprehensive characterization of each binder's behaviour at low temperature, three measurements were repeated at different temperatures to determine the fracture toughness temperature ( $T_{\text{FTT}}$ ). Different temperatures were tested, from  $-15^{\circ}\text{C}$  to  $0^{\circ}\text{C}$  and the corresponding  $T_{\text{FTT}}$  was calculated. As depicted in Figure 10, increasing the temperature tends to increase the deflection, as the material gets tougher.

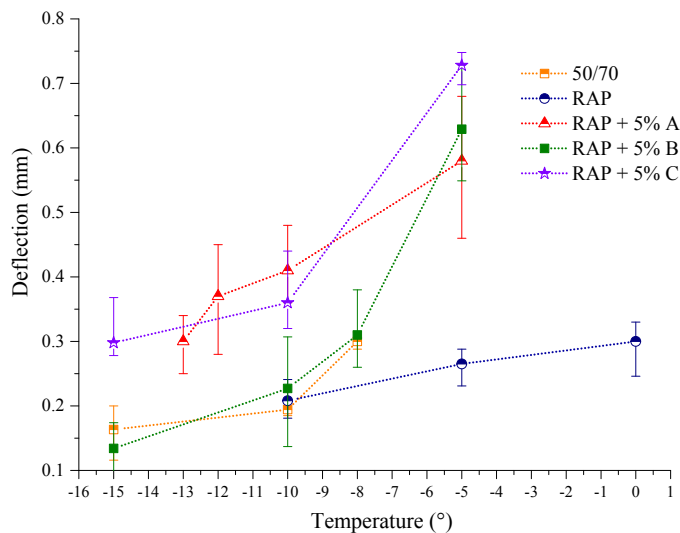


Figure 10 Deflection variation with temperature for all the binders tested at unaged state. Standard deviation was calculated for four measurements per sample.

As shown in Figure 11, RAP binder starts cracking around  $-1^{\circ}\text{C}$ . By adding rejuvenators, low temperature fracture of RAP binder decreases. RAP + 5% A presented a  $T_{\text{FTT}}$  equal to  $-13^{\circ}\text{C}$  ( $12^{\circ}\text{C}$  lower than RAP binder) while RAP + 5% B showed a  $T_{\text{FTT}}$  of  $-10^{\circ}\text{C}$  and RAP + 5% C reached the prescribed displacement at  $-15^{\circ}\text{C}$ . For all rejuvenated binders it was possible to observe that cracks appear at a lower temperature compared to the neat RAP binder. In particular, rejuvenator A and C could decrease the RAP binder's  $T_{\text{FTT}}$  by  $12^{\circ}\text{C}$  and  $14^{\circ}\text{C}$  compared to the unaged RAP binder. On the contrary, rejuvenator B could decrease the RAP binder's  $T_{\text{FTT}}$  by  $9^{\circ}\text{C}$ . By investigation of the materials at aged state, a general tendency can be seen: aging causes an increase of  $T_{\text{FTT}}$  for all the binders. It can be observed how RAP + 5% A and RAP + 5% C increased their  $T_{\text{FTT}}$  with respect to their unaged state, by about  $3^{\circ}\text{C}$  and  $4^{\circ}\text{C}$  respectively while RAP + 5% B showed an increase of  $2^{\circ}\text{C}$ .

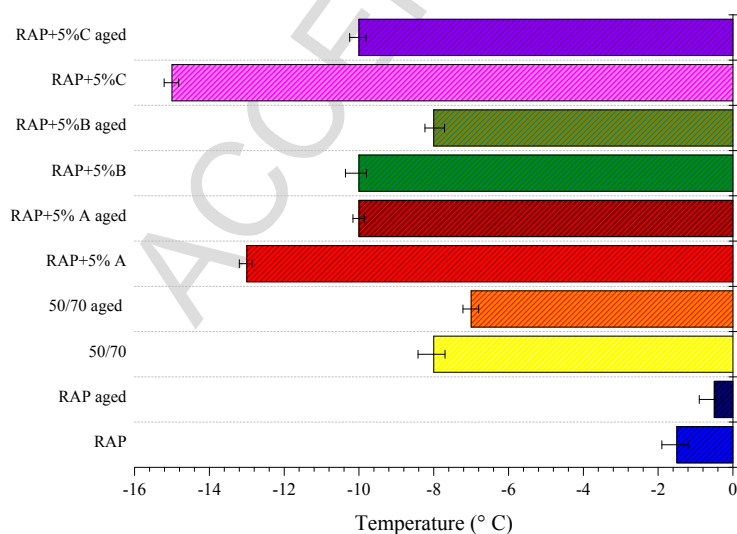


Figure 11 Fracture toughness temperature for the different materials at unaged/aged state. Average and Standard deviation was calculated for four measurements.

### 3.3 Rheological measurements

In order to investigate the material's response to temperature changes, a study of the rheological properties of asphalt binders was conducted. As can be seen in Figure 12, RAP binder has lower phase angle and higher complex moduli at unaged state than the other binders. By adding 5% of each rejuvenator, the complex moduli at unaged state decreased for all the frequencies range by one order of magnitude (for RAP+ 5% A) to two orders of magnitude (RAP+5% C). The phase angle increased, especially at low temperature; e.g. for RAP+5% B at  $-10^{\circ}\text{C}$  it showed an increase of  $20^{\circ}$  with respect to the RAP binder (phase angle close to  $15^{\circ}$ ). These results show that the relationship between  $G'$  and  $G''$  can be controlled by the rejuvenators used in this study. Moreover, at  $-10^{\circ}\text{C}$ , rejuvenators contributed to increase of the phase angle. This corresponds to an increase of  $G''$ , which is desirable. At aged state, the curves of the all materials master curves tend to merge at all frequency ranges. After aging, RAP + 5% B had the highest complex moduli and lowest phase angles, even as compared to RAP binder with no rejuvenators, which indicated that the softening effect observed in the unaged state was no longer present. On the contrary, RAP + 5% A and RAP + 5% C maintained both complex moduli and phase angle at a level similar to the aged virgin binder due to a significant difference in the rejuvenating effect after aging. Generally, from results presented in the previous section, it can be stated that rejuvenators A and C were able to restore the fracture toughness of RAP binder to a larger extend than B. This resulted also in an increase of the phase angle.

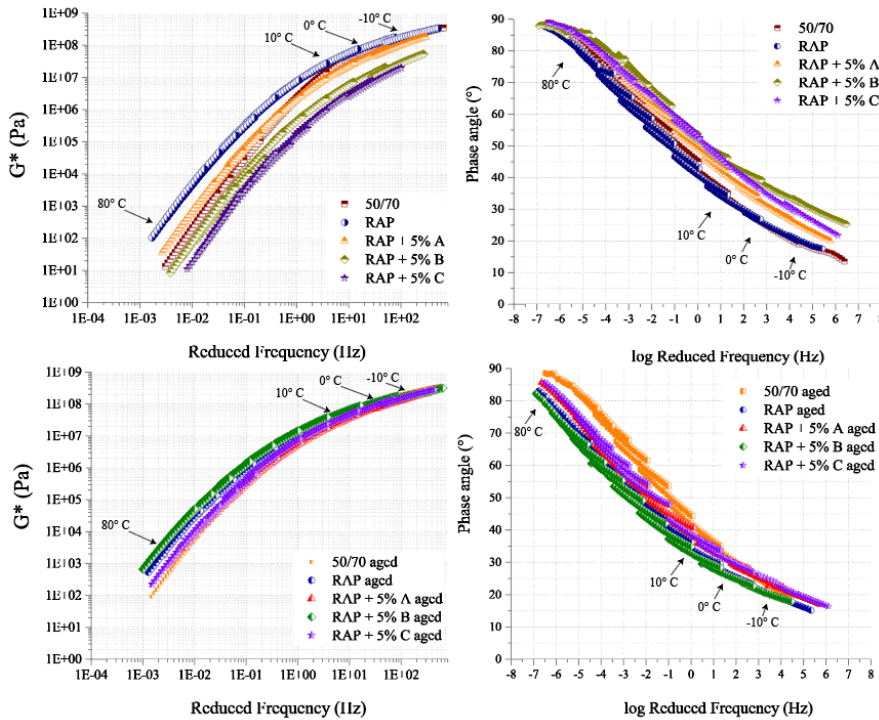


Figure 12 Modulus and phase angle master curves for all the unaged binders (on top) and the aged ones (on the bottom). Values presented are averages of four measurements.

At low temperatures bituminous binders are known to be more elastic ( $G' > G''$ ) whereas at high temperatures the opposite is true. As shown in the example in Figure 13, the interplay between the elastic and viscous component of the complex modulus undergoes a change at a precise frequency. Defining a so called “crossover frequency” at which this transition occurs can provide a measure of the dissipative behaviour of the material (Asgharzadeh et al., 2013). As a general trend, the higher the crossover frequency, the more viscous response the material will show. High crossover frequency at low temperature indicates a better cracking resistance.

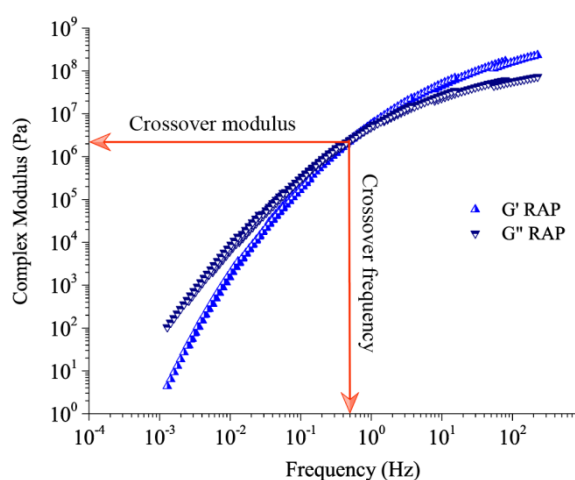


Figure 13 Example of elastic and viscous components of the complex modulus ( $G'$ ,  $G''$ ) together with the crossover frequency. The data plotted are average of four measurements.

Results in Figure 14 (in log-log scale) indicate that the rejuvenators of this study could restore the crossover frequency of RAP binder. Nevertheless, aging had a significant effect in lowering the crossover frequency. For RAP binder, RAP + 5% A and RAP + 5% B, the transition between elastic and viscous portion appears at lower crossover frequency compared to virgin 50/70 and RAP + 5% C. Generally, it can be seen how for the modified RAP binders, aging was associated to a frequency shift rather than a change in terms of crossover moduli.

In particular, crossover frequency decreases for all the binders after aging. On the contrary, after aging, the crossover modulus which is obtained when  $G'$  is equal to  $G''$ , do not show a unique trend for all the materials. If the crossover modulus decreases, it can indicate that at the corresponding crossover frequency the binder has softened. However, the material may have stiffened (as for example for the virgin binder). Moreover, when the crossover modulus increases, aging is very prominent and its frequency dependency has been strongly reduced (resulting in flatter master curve as shown in Figure 12). If the crossover modulus decreases after aging, the effect of aging in terms of reduction of frequency dependency is less prominent. It is hereby assumed that the RAP binder stiffened due to aging, but it kept its frequency dependency. Whereas in the case of the virgin binder

50/70, a general reduction of the frequency dependency was observed. In conclusion, RAP + 5% A showed to be less affected by aging as both crossover frequency and crossover modulus show comparatively flat change after aging.

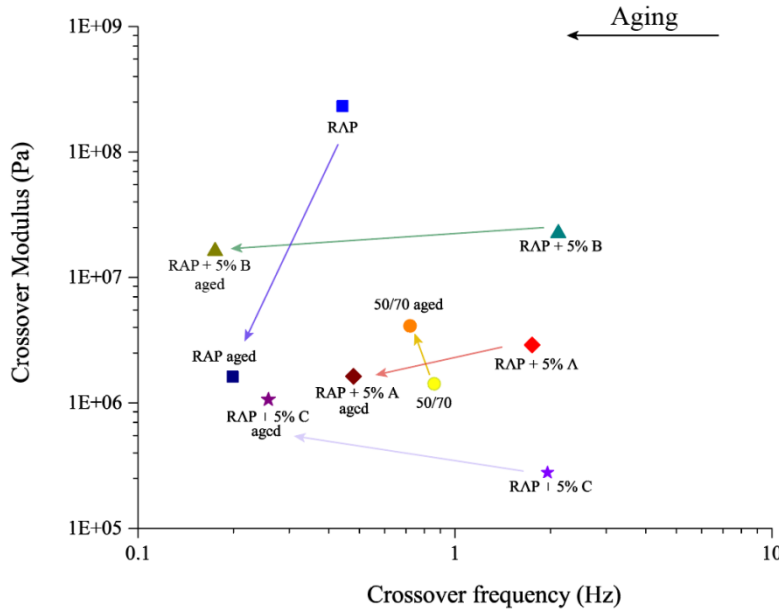


Figure 14 Crossover modulus and crossover frequency (log-log scale) for all materials tested before and after aging.

#### 4. Conclusions

Low temperature is one of the most important climatic factors influencing the conditions of pavements with RAP and it plays a key role in crack initiation. Cracking behaviour at low temperature together with rheological measurements were performed and the effect of aging on the effectiveness of three different bio-based rejuvenators was evaluated. By combining rheological measurements and FTT analysis the effectiveness of rejuvenators in restoring the properties of the RAP binder is shown. The main findings from the fracture toughness tests were:

- Rejuvenators had a positive effect on the unaged RAP binder: fracture toughness temperature ( $T_{FTT}$ ) decreased after the addition of 5% rejuvenator and this decrease was rejuvenator dependent.
- After aging, the fracture toughness temperature,  $T_{FTT}$  of RAP + 5% A and RAP + 5% C was lower than aged RAP + 5% B. In particular, rejuvenators A and C showed better performances in restoring the RAP's binder rather than rejuvenator B.
- Work of fracture at  $-10^{\circ}\text{C}$  showed a significant improvement in the ductile behaviour of RAP binder after the addition of rejuvenators, both before and after aging.

The main findings from the rheological and chemical studies are:

- By adding 5% of each bio-based product, modified RAP binder had rheological performances similar to the virgin binder at low temperature. RAP + 5% B and RAP + 5% C showed higher softening potential of the RAP binder in the entire frequencies/temperature range compared to RAP + 5% A.
- After aging, RAP + 5% A and RAP + 5% C had similar mechanical performances to the aged virgin binder in the entire frequency/temperature range. An increase in the phase angle and a shift of crossover frequency were found after addition of rejuvenators. RAP + 5% B was more influenced by aging than the other rejuvenated binders and had a lower crossover frequency than the RAP binder itself.
- Aging had a significant effect in lowering the crossover frequency. For RAP binder, RAP + 5% A and RAP + 5% B, the transition between elastic and viscous portion was seen at lower crossover frequency compared to virgin 50/70 and RAP + 5% C. Generally, it can be seen how for the modified RAP binders, aging was associated to a frequency shift rather than a change in terms of crossover moduli.
- Rejuvenators could mechanically restore the aged RAP binder showing significant differences in the modulus and phase angle results. In addition, it has been shown how mechanical changes due to rejuvenators were not caused by changes at chemical bonds/functional groups level.

### Acknowledgments

This research was funded by the Swiss federal office for the environment grant number UTF 489.19.14 / IDM 2006.2423.487

### References

- Airey, G.D., Rahimzadeh, B., Collop, A.C., 2004. Linear Rheological Behavior of Bituminous Paving Materials. *J. Mater. Civ. Eng.* 16, 212–220. doi:10.1061/(ASCE)0899-1561(2004)16:3(212)
- Ali, A.W., Mehta, Y.A., Nolan, A., Purdy, C., Bennert, T., 2016. Investigation of the impacts of aging and RAP percentages on effectiveness of asphalt binder rejuvenators. *Constr. Build. Mater.* 110, 211–217. doi:10.1016/j.conbuildmat.2016.02.013
- Anderson, D., Lapalu, L., Marasteanu, M., Hir, Y., Planche, J.-P., Martin, D., 2001. Low-Temperature Thermal Cracking of Asphalt Binders as Ranked by Strength and Fracture Properties. *Transp. Res. Rec.* 1766, 1–6. doi:10.3141/1766-01
- Asgharzadeh, S.M., Tabatabaee, N., Naderi, K., Partl, M., 2013. An empirical model for modified

- bituminous binder master curves. *Mater. Struct.* 46, 1459–1471. doi:10.1617/s11527-012-9988-x
- Baek, S.-H., Hong, J.-P., Kim, S.U., Choi, J.-S., Kim, K.-W., 2011. Evaluation of Fracture Toughness of Semirigid Asphalt Concretes at Low Temperatures. *Transp. Res. Rec. J. Transp. Res. Board* 2210, 30–36. doi:10.3141/2210-04
- Bueno, M., Hugener, M., Partl, M.N., 2015. Fracture toughness evaluation of bituminous binders at low temperatures. *Mater. Struct.* 48, 3049–3058. doi:10.1617/s11527-014-0378-4
- Cannone Falchetto, A., Turos, M.I., Marasteanu, M.O., 2012. Investigation on asphalt binder strength at low temperatures. *Road Mater. Pavement Des.* 13, 804–816. doi:10.1080/14680629.2012.735793
- Cavalli, M.C., Partl, M.N., Poulikakos, L.D., 2017. Measuring the binder film residues on black rock in mixtures with high amounts of reclaimed asphalt. *J. Clean. Prod.* 149, 665–672. doi:10.1016/j.jclepro.2017.02.055
- Cavalli, M.C., Zaumanis, M., Mazza, E., Partl, M.N., Poulikakos, L.D., 2018. Effect of ageing on the mechanical and chemical properties of binder from RAP treated with bio-based rejuvenators. *Compos. Part B Eng.* 141, 174–181. doi:10.1016/j.compositesb.2017.12.060
- Dedene, C.D., You, Z., 1997. The Performance of Aged Asphalt Materials Rejuvenated with Waste Engine Oil. *ISSN Int. J. Pavement Res. Technol. Int. J. Pavement Res. Technol.* 77, 145–152. doi:10.6135/ijprt.org.tw/2014.7(2).145
- Dondi, G., Mazzotta, F., Simone, A., Vignali, V., Sangiorgi, C., Lantieri, C., 2016. Evaluation of different short term aging procedures with neat, warm and modified binders. *Constr. Build. Mater.* 106, 282–289. doi:10.1016/j.conbuildmat.2015.12.122
- European Committee for Standardization CEN, 2010. CEN TS15963. Bitumen and bituminous binders. Determination of the fracture toughness temperature by a three point bending test on a notched specimen.
- EUROPEAN STANDARD 12697-1 Bituminous mixtures - Test methods for hot mix asphalt - Part 1: Soluble binder content., 2012.
- EUROPEAN STANDARD 14769:2012: Bitumen and bituminous binders - Accelerated long-term ageing conditioning by a Pressure Ageing Vessel (PAV), 2012. 16.
- EUROPEAN STANDARD EN 12607-1: Bitumen and bituminous binders — Determination of the resistance to hardening under the influence of heat and air —, 2007. 3, 1–15.
- EUROPEAN STANDARD EN 1426: Determination of the needle penetration, 2012.
- EUROPEAN STANDARD EN 14770: Bitumen and bituminous binders — Determination of complex shear modulus and phase angle — Dynamic Shear Rheometer ( DSR ), 2012. 1–22.
- Gergesova, M., Zupančič, B., Saprunov, I., Emri, I., 2011. The closed form t-T-P shifting (CFS) algorithm. *J. Rheol. (N. Y. N. Y.)* 55, 1. doi:10.1122/1.3503529

- Hoon Moon, K., Cannone Falchetto, A., Wang, D., Wistuba, M.P., Tebaldi, G., 2017. Low-temperature performance of recycled asphalt mixtures under static and oscillatory loading. *Road Mater. Pavement Des.* 18, 297–314. doi:10.1080/14680629.2016.1213500
- Huang, S.C., Qin, Q., Grimes, R.W., Pauli, A.T., Glaser, R., 2015. Influence of rejuvenators on the physical properties of RAP binders 43, 594–603. doi:10.1520/JTE20130314
- Ji, J., Yao, H., Suo, Z., You, Z., Li, H., Xu, S., Sun, L., 2017. Effectiveness of Vegetable Oils as Rejuvenators for Aged Asphalt Binders. *J. Mater. Civ. Eng.* 29, D4016003. doi:10.1061/(ASCE)MT.1943-5533.0001769
- Jia, X., Huang, B., Bowers, B.F., Zhao, S., 2014. Infrared spectra and rheological properties of asphalt cement containing waste engine oil residues. *Constr. Build. Mater.* 50, 683–691. doi:10.1016/J.CONBUILDMAT.2013.10.012
- Kang, H., Tang, Y., Yao, L., Yang, F., Fang, Q., Hui, D., 2017. Fabrication of graphene/natural rubber nanocomposites with high dynamic properties through convenient mechanical mixing. *Compos. Part B Eng.* 112, 1–7. doi:10.1016/j.compositesb.2016.12.035
- Karen, P., McArdle, P., Takats, J., 2016. Comprehensive definition of oxidation state (IUPAC Recommendations 2016). *Pure Appl. Chem.* 88, 831–839. doi:10.1515/pac-2015-1204
- Lamontagne, J., Durrieu, F., Planche, J.P., Mouillet, V., Kister, J., 2001. Direct and continuous methodological approach to study the ageing of fossil organic material by infrared microspectrometry imaging: Application to polymer modified bitumen. *Anal. Chim. Acta* 444, 241–250. doi:10.1016/S0003-2670(01)01235-1
- Leng, Z., Padhan, R.K., Sreeram, A., 2018. Production of a sustainable paving material through chemical recycling of waste PET into crumb rubber modified asphalt. *J. Clean. Prod.* 180, 682–688. doi:10.1016/J.JCLEPRO.2018.01.171
- Li, X., Marasteanu, M.O., Williams, R.C., Clyne, T.R., 2008. Effect of Reclaimed asphalt Pavement (Proportion and Type) and Binder Grade on Asphalt Mixtures. *Transp. Res. Rec. J. Transp. Res. Board* 2051, 90–97. doi:10.3141/2051-11
- Lopes, M., Mouillet, V., Bernucci, L., Gabet, T., 2016. The potential of Attenuated Total Reflection imaging in the mid-infrared for the study of recycled asphalt mixtures. *Constr. Build. Mater.* 124, 1120–1131. doi:10.1016/j.conbuildmat.2016.08.108
- Mangiafico, S., Sauzéat, C., Benedetto, H. Di, Pouget, S., Olard, F., 2015. Influence of a recycling agent of vegetable origin on complex modulus and fatigue performances of bituminous mixtures produced with Reclaimed Asphalt Pavement 629, 1–14. doi:10.1080/14680629.2016.1213509
- Menon, A.R.R., Pillai, C.K.S., Mathew, A.G., 1985. CASHEWNUT SHELL LIQUID - ITS POLYMERIC AND OTHER INDUSTRIAL PRODUCTS. *J. Sci. Ind. Res. (India)*. 44, 324–338.
- Mousavi, M., Pahlavan, F., Oldham, D., Hosseinneshad, S., Fini, E.H., 2016. Multiscale Investigation

- of Oxidative Aging in Biomodified Asphalt Binder. *J. Phys. Chem.*  
doi:10.1021/acs.jpcc.6b05004
- Ongel, A., Hugener, M., 2015. Impact of rejuvenators on aging properties of bitumen. *Constr. Build. Mater.* 94, 467–474. doi:10.1016/j.conbuildmat.2015.07.030
- Petersen, J.C., Glaser, R., 2011. Asphalt Oxidation Mechanisms and the Role of Oxidation Products on Age Hardening Revisited. *Road Mater. Pavement Des.* 12, 795–819.  
doi:10.1080/14680629.2011.9713895
- Qurashi, I.A., Swamy, A.K., 2018. Viscoelastic properties of recycled asphalt binder containing waste engine oil. *J. Clean. Prod.* 182, 992–1000. doi:10.1016/J.JCLEPRO.2018.01.237
- Raman, N.A.A., Hainin, M.R., Hassan, N.A., Ani, F.N., 2015. A review on the application of bio-oil as an additive for asphalt. *J. Teknol.* 72, 105–110. doi:10.11113/jt.v72.3948
- Ritchie, R.O., 2011. The conflicts between strength and toughness. *Nat. Mater.* 10, 817–822.  
doi:10.1038/nmat3115
- Sun, D., Lu, T., Xiao, F., Zhu, X., Sun, G., 2017. Formulation and aging resistance of modified bio-asphalt containing high percentage of waste cooking oil residues. *J. Clean. Prod.*  
doi:10.1016/j.jclepro.2017.06.155
- Williams, M.L., Landel, R.F., Ferry, J.D., 1955. The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids. *J. Am. Chem. Soc.* 77, 3701–3707. doi:10.1021/ja01619a008
- Witczak, M., Fonseca, O., 1996. Revised Predictive Model for Dynamic (Complex) Modulus of Asphalt Mixtures. *Transp. Res. Rec.* 1540, 15–23. doi:10.3141/1540-03
- Yang, X., Mills-Beale, J., You, Z., 2017. Chemical characterization and oxidative aging of bio-asphalt and its compatibility with petroleum asphalt. *J. Clean. Prod.* 142, 1837–1847.  
doi:10.1016/j.jclepro.2016.11.100
- Zaumanis, M., Mallick, R.B., Frank, R., 2014. Determining optimum rejuvenator dose for asphalt recycling based on Superpave performance grade specifications. *Constr. Build. Mater.* 69, 155–166. doi:10.1016/j.conbuildmat.2014.07.035
- Zhang, R., Wang, H., You, Z., Jiang, X., Yang, X., 2017. Optimization of bio-asphalt using bio-oil and distilled water. *J. Clean. Prod.* 165, 281–289. doi:10.1016/J.JCLEPRO.2017.07.154
- Zhu, H., Xu, G., Gong, M., Yang, J., 2017. Recycling long-term-aged asphalts using bio-binder/plasticizer-based rejuvenator. *Constr. Build. Mater.* 147, 117–129.  
doi:10.1016/J.CONBUILDMAT.2017.04.066

- Fracture toughness transition temperature of RAP decreases after the addition of rejuvenators.
- After the addition of rejuvenators, work up to fracture of RAP improves.
- Bio-based rejuvenators are able to restore the mechanical properties of RAP binder.
- The viscoelastic characteristics depend on ageing and can be influenced by RAP's rejuvenators.
- Mechanical changes due to rejuvenators were not caused by changes at chemical bonds/functional groups level.

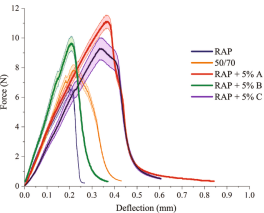


RAP binder



Bio-based rejuvenators

Cracking behaviour



Rheology

