CHEMICAL ENGINEERING TRANSACTIONS
VOL. 86, 2021
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6; **ISSN** 2283-9216
DOI: 10.3303/CET2186209

Use of Recycled Oils as Rejuvenators for Bituminous Binders

Norma Mallegni, Miriam Cappello, Sara Filippi*, Pietro Leandri, Giovanni Polacco, Massimo Losa

Dept. Of Civil and Industrial Engineering, University of Pisa Largo Lucio Lazzarino, 1, 56122 Pisa - Italy
sara.filippi@unipi.it

The addition of rejuvenators agents (RJ) into bitumen allows increasing the amount of recycled asphalt in new mixtures. In the preliminary part of this study, three different type of oils were tested as potentials RJ: a mineral oil from the automotive industry, a waste domestic cooking vegetable oil (VO), and a biodiesel. Several mixtures were prepared by adding different percentage of oils and VO was individuated as the best RJ. Therefore, VO was used in a further investigation, to better characterize the properties of the rejuvenated binder and its resistance to aging during a second life cycle. Rejuvenated binders with different oil content were prepared and evaluated. The rheological characterization included frequency sweep tests to obtain the binder master curves and linear amplitude sweep test to evaluate the cumulative damage resistance. Moreover, the molecular weight distributions of the binders were investigated by both gel permeation chromatography and rheology by application of the delta-method.

1. Introduction

In the past years, the use of reclaimed asphalt pavement (RAP) has globally become an important strategy in the preparation of new roads. This growth in interest is motivated by many reasons like costs reduction, use of eco-friendly solutions and energy efficiency. Of course, the recycled binder has been subjected to oxidative aging that determines a physical hardening and limits its workability and performances like i.e. the cracking susceptibility. For this reason, low molecular weight rejuvenators (RJ) have been introduced to restore the original viscosity and properties, thus allowing an increase in the percentage of RAP in the new formulations. Many kind of RJ have been suggested and the interested reader may find an up to date state of the art in the reviews of Benhood (2019) and Zhang et al. (2020). Since the rejuvenated binder is supposed to have a second life cycle, the selection of an appropriate rejuvenator is of critical importance. First of all, the RJ must be fully compatible with the bituminous binder and remain in the binder during the in-service life without undergoing phase separation phenomena. Second, the RJ must have a high diffusivity in the binder, to homogeneously distribute in it during the very short mixing time usually adopted in the laying of the road. Third, the RJ must guarantee a full restoring of the binder properties and pavement durability.
Based on these three aspects, in a previous study a waste domestic cooking vegetable oil (VO) was selected as the most promising one among three different oils including a mineral oil from the automotive industry and a biodiesel. However, for a full validation of VO as a suitable RJ, there are two other important aspects that deserve attention and have been the subject of this work: individuate the optimal quantity of RJ and evaluate the aging resistance during the second life of the recycled binder. For this purpose, a base bitumen was artificially aged and then regenerated by using different quantities of VO. The rejuvenated binders were then further aged in order to compare the aging resistance of the original and rejuvenated binders. All the materials were subjected to rheological characterization based on isothermal frequency sweep tests to obtain the binder master curves and linear amplitude sweep test to evaluate the cumulative damage resistance. Moreover, the molecular weight distributions (and degree of aggregation between the molecules) were evaluated both in bulk and diluted conditions.

Paper Received: 29 August 2020; Revised: 30 January 2021; Accepted: 28 April 2021
Please cite this article as: Mallegni N., Cappello M., Filippi S., Leandri P., Polacco G., Losa M., 2021, Use of Recycled Oils as Rejuvenators for Bituminous Binders, Chemical Engineering Transactions, 86, 1249-1254 DOI:10.3303/CET2186209

2. Experimental

The base binder (B) was a bitumen with Penetration grade 50-70 kindly furnished by ENI. The VO is a domestic waste vegetable oil, from which food particles and water were previously removed by filtering and decanting. The short and long term artificial aging of the original and rejuvenated binders were conducted by Rolling Thin Film Oven (RTFO – UNI EN 12607-1) and Pressure Aging Vessel (PAV – AASHTO R28) respectively. The rejuvenated blends were obtained by mixing the PAV aged bitumen with weighed amounts of VO: approximately 70 g of bitumen were heated at 140 ± 5°C and subjected to gently stirring to homogenise the composition and temperature profile of the sample. After a few minutes, the oil was added and the blend left under stirring (200 rpm) for further 30 minutes. Blends with 2.5, 3, 3.5 and 4% by weight of VO were prepared. In what follows the unaged, RTFO aged and PAV aged binder will be indicated as B-U, B-RTFO and B-PAV respectively. The rejuvenated blends will be indicated as B-XVO-aging, where X is the VO content and “aging”, if present is either U, RTFO or PAV. As an example, B-3.5VO-PAV is the blend of B-PAV with 3.5% by weight of rejuvenator after the second PAV aging procedure.

All rheological tests were performed by using a Malvern Kinexus PRO Dynamic Shear Rheometer (DSR). The frequency sweep tests were conducted under isothermal condition within the linear viscoelastic region to generate the master curves. Parallel plate geometry with 8 mm diameter and 2 mm gap was used in the -10 to 30 °C temperature range, while 25 mm plate with 1.2 mm gap was used in the 30 to 70 °C range. The loading frequency varied from 0.1 to 10 Hz and the master curves were built at 0°C reference temperature by applying the time temperature superposition principle. Master curves have been used to calculate the so-called apparent molecular weight distribution (AMWD) by using the δ-method, recently developed by Themeli et al. (2015) and subsequently revised by Cuciniello et al. (2020). The method is based on the idea that the dimension of the single molecules is directly linked with their relaxation frequencies and to their contribution to the phase angle of the material. Therefore, a relation between molecular weight and reduced frequency allows transforming the phase angle master curve in a cumulative molecular weight distribution. A fitting of the master curves by using the 2S2P1D model (Yusoff et al., 2010) allowed an easier mathematical manipulation of the data to obtain the AMWD. Distributions derived from rheological data are referred as “apparent” to underline that the use of bulk measurement, takes into account both molecular weight and interactions with the surrounding molecules. In other words, the distribution considers as a unique entity an aggregation of molecules.

Linear Amplitude Sweep (LAS) was used to estimate the damage tolerance of the binders, according to AASHTO TP 101-14. Samples were tested in an 8-mm-diameter parallel plate geometry with 2-mm gap setting. The test starts with a frequency sweep in the 0.2–30.0 Hz range at a fixed load (0.1% strain), followed by an amplitude sweep with steps every 1% until 30%. Each step includes 100 cycles so that cumulatively the material is subjected to 3100 cycles. The LAS test should be performed at an intermediate temperature according to the PG grade of the binder. In our case, the chosen temperature was 25°C with two replicates for each sample. The LAS tests gives three parameters as a final result: N_f, A and B. N_f represents the number of cycles to failure, defined as 35% reduction in the initial modulus. A and B are coefficients that depend on the material characteristics. A parameter represents the materials ability to keep its integrity during loading cycles and due to accumulated damage and it is directly related to the storage modulus. B parameter is the sensitivity of the asphalt binder to strain level change, higher absolute values of B parameter indicates that the fatigue life decreases at a higher rate when strain level amplitude increases. Generally, more fatigue resistant binders have higher A and lower absolute B values (Sabouri et al., 2018).

The Gel Permeation Chromatography (GPC) was performed with a GPC from Jasco, equipped with a Refractive Index detector RI-4030 and UV/Vis detector UV-4070. The column was a Phenogel, 5 μm, pore size 10^3 Å, designed for molecular weights from 1000 to 75,000 Da. The injected volume was 8 μL, the solvent (Tetrahydrofuran) flow rate was 2 mL/min and the column was set at a temperature of 25°C. All samples were filtered through a 0.45 μm PTFE filters.

3. Results and Discussion

In the GPC analysis, all the samples showed a retention time interval between 3 and 6 minutes, which are not compatible with the retention times obtained with the use of polystyrene standards. In other words, the application of a calibration curve, based on polystyrene would give very low and even negative molecular weights in the case of bitumen. This means that there are interactions between the oxygen-containing functional groups of the bitumen molecules and the column. Since the oxidative aging increases the number of such groups, GPC can be used as an effective tool to evaluate the aging effects. As an example, Figure 1 (left) shows the GPC curves of B before and after artificial aging. The GPC curve is basically composed of two main peaks. The first one (lower retention time, higher molecular weights) can be attributed to resins and asphaltenes, while the second one (higher retention time, lower molecular weights) to maltenes. As expected and well documented in the literature (Petersen, 2011), the oxidative aging determines the shift of a portion of maltenes into the resin-asphaltenes family. This is the reason why after PAV there is an increase in the population belonging to the first peak and a parallel reduction in the second peak. Figure 1 (right) shows the B-PAV before and after addition of RJ, which is responsible for the small peak around 4.6 min retention time (as visible from the blue curve, corresponding to the VO alone and reported in a reduced y-axis scale).

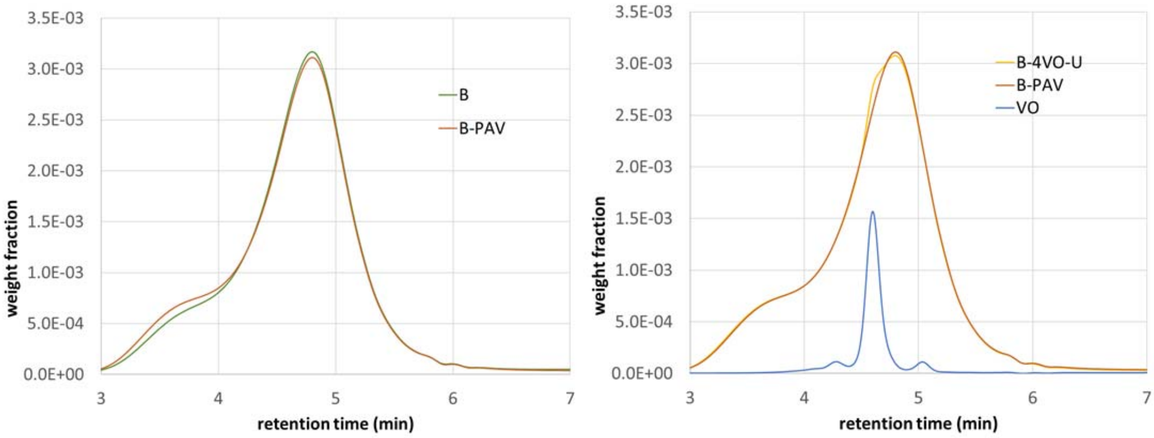

Figure 1: GPC curves of: binder B before and after PAV aging (left); binder B-PAV before and after addition of the RJ (right). The blue curve is the distribution of retention times for the VO alone and has been represented in a reduced scale (in order to be conveniently represented in the same graph).

Figure 2 (left) is analogous to Figure 1, but shows the effect of aging on a rejuvenated binder (the one with the higher oil content). Finally, Figure 2 (right) shows a comparison of the curves after PAV aging for the original and rejuvenated binder.

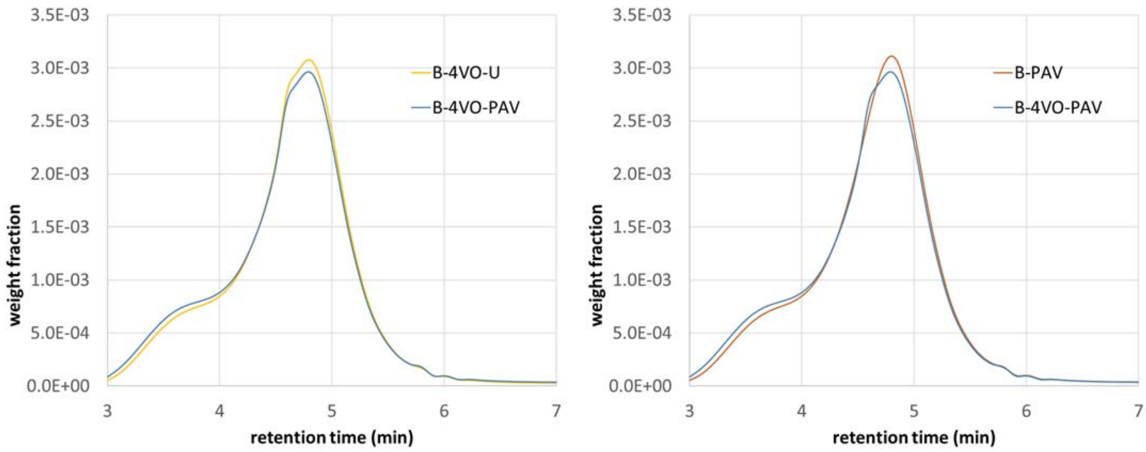

Figure 2: GPC curves of binder B-4VO before and after PAV aging (left); comparison of binders B-PAV and B-4VO-PAV (right).

The GPC curves can be used to calculate an aging index, i.e. by quantifying the relative area of the two populations, which is easier after a simple deconvolution procedure to fit the curve as a sum of Gaussian distributions. This procedure was applied to all the blends and results (not reported here for the sake of brevity) showed that there are no significant differences between the aging of the base binder and that of its rejuvenated forms. This is not surprising, since the addition of the oil does not alter the chemistry of the binder and neither its reactivity with respect to oxygen. Moreover, the molecular weight distributions obtained with GPC in dilute conditions are similar for all samples, because aging consists in a partial oxidation of the molecules and do not affects significantly the molecular weight of the molecules. In contrast, oxidation alters the polarity of the molecules and thus their degree of interactions with the surrounding molecules. This is hidden by the presence of the solvent in case of GPC, but should be well visible in bulk measurement. For this reason, it is interesting to calculate the AMWD by using the δ-method.

Figure 3 (left) shows the AMWD for the base bitumen before and after artificial aging. The first observation is that aging has a much higher impact on the distribution curves with respect to the case of GPC. In particular, aging determines a shift of the right part of the distributions toward higher molecular weights. Moreover, there is a decrease of the low molecular weight peaks in favour of those at high molecular weights. This is coherent with the above-mentioned increased interaction between molecules and indicate a higher content and aggregation of resins and asphaltenes, the populations containing the oxidised functional groups. A comparison of aged (B-PAV) and rejuvenated (B-4VO-U) binders (Figure 3 right) indicates that the RJ, in spite of its almost fixed molecular weight, has a strong effect on the whole distribution. In particular, it is able to restore the original degree of aggregation of the heaviest molecules. This is confirmed by the comparison of the original unaged (B-U) and rejuvenated binder (B-4VO-U) whose right end side of the distributions perfectly overlaps (Figure 4 left). Finally, it is interesting to observe that the distributions of B-PAV and B-4VO-PAV are very similar (Figure 4 right). This is a further indication that RJ allows a second life cycle comparable to the first one.

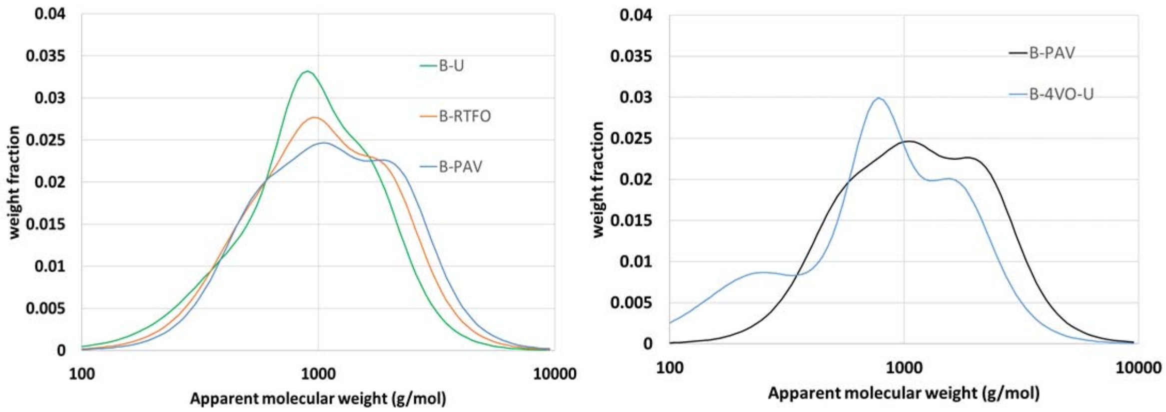

Figure 3: AMWD of the original binder at different levels of aging (left) and comparison of the distributions before and after addition of RJ (right).

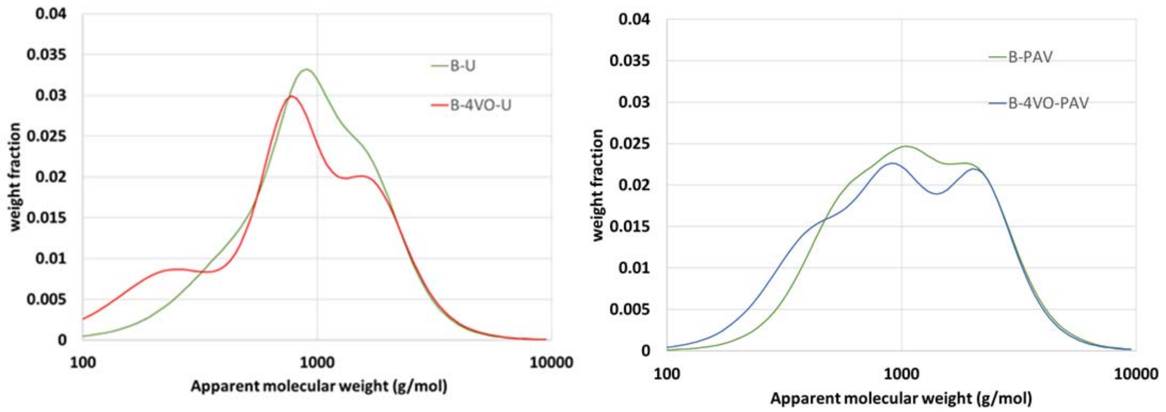

Figure 4: Comparison of the AMWD of the original binder and of the rejuvenated binder (left) and of the binder at the end of the first and second simulated life cycle (right).

Figure 5 (left) shows the effect of different percentages of RJ on the phase angle master curves. It can be seen that the curve relative to the original binder crosses all the other curves, thus evidencing that the softening effect of the oil is more pronounced in the high frequency (low temperature) range. Moreover, the behaviour of B-U is better restored with high oil content in the low frequency range and lower oil content in the medium-high range. With regard to the magnitude of the complex modulus (G*), Figure 5 (right) allows observing the effect of the different percentages of RJ. A similar qualitative behaviour is observed after RTFO aging of the binders (Figure 6), but the differences among the master curves results reduced with respect to the previous case (Figure 5). This indicates that the VO has a tendency to evaporation during RTFO and thus after laying the rejuvenated binder have a rheological behaviour closest to that of the original binder.

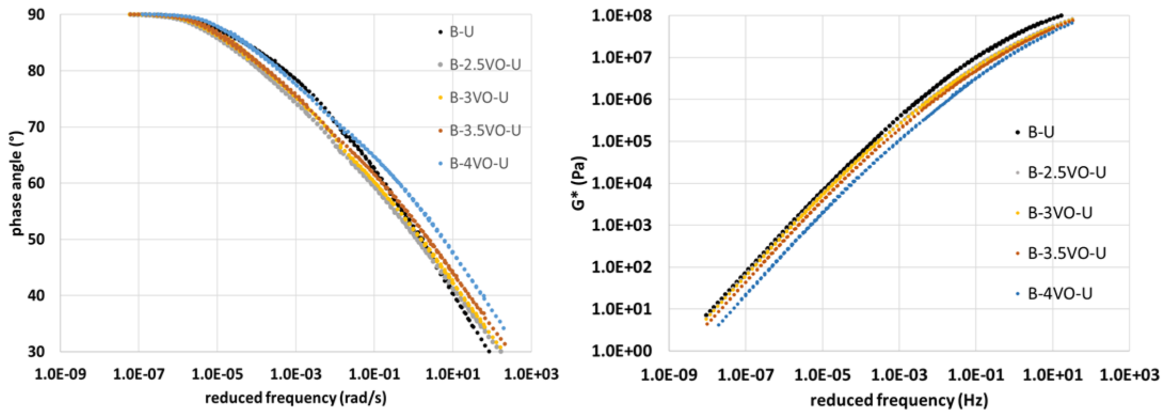

Figure 5 Phase angle (left) and magnitude of complex modulus (right) master curves of the unaged original and rejuvenated binders.

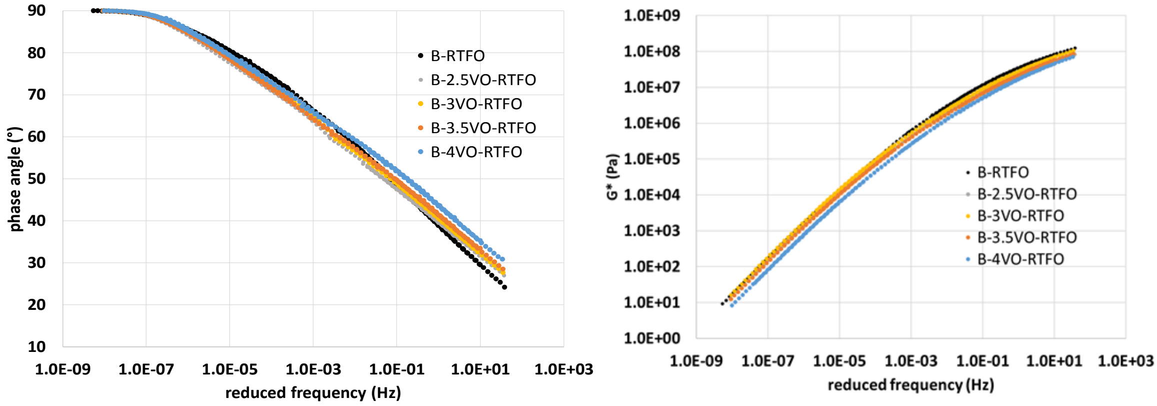

Figure 6 Phase angle (left) and magnitude of complex modulus (right) master curves of the RTFO aged original and rejuvenated binders.

The LAS test was used to evaluate the effects of laboratory-simulated aging on the cumulative damage resistance of the original and rejuvenated binders. Table 1 shows the obtained results for all the artificially aged blends. The number of cycles to failure (N_f) have been calculated at two strain levels: 2.5 and 5.0 %, representative of strong (or thick) and weak (or thin) pavements respectively. As expected, an increase in oil percentage softens the binder and thus leads to an increase in fatigue resistance (higher values of N_f and A and lower values of B). However, a too soft material would be subjected to rutting and thus the optimal oil content must take into account also this aspect. A comparison with the unmodified binder properties, suggests that 2.5 is the percentage of oil that better reproduces the original properties.

Table 1: LAS results

Sample	N_f 2.5%	N_f 5%	A	B
B-RTFO	4.03E+03	6.84E+02	4.20E+04	2.56E+00
B-2.5VO-RTFO	4.43E+03	5.54E+02	6.94E+04	3.00E+00
B-3VO-RTFO	4.72E+03	6.37E+02	6.66E+04	2.89E+00
B-3.5VO-RTFO	8.57E+03	1.14E+03	1.24E+05	2.92E+00
B-4VO-RTFO	9.02E+03	1.23E+03	1.25E+05	2.87E+00
B-PAV	4.35E+03	5.43E+02	6.83E+04	3.02E+00
B-2.5VO-PAV	4.92E+03	5.33E+02	9.28E+04	3.21E+00
B-3VO-PAV	5.34E+03	5.92E+02	9.80E+04	3.18E+00
B-3.5VO-PAV	5.61E+03	6.80E+02	9.12E+04	3.05E+00
B-4VO-PAV	7.16E+03	8.70E+02	1.23E+05	3.07E+00

4. Conclusions

The use of rejuvenators is an interesting approach in the recycle of asphalt pavements that have been deteriorated by aging. Rejuvenators are small molecular weight oils that reduce the effects of stiffening and increased viscosity undergone by the binder thus restoring its workability. However, after laying, the new pavement must guarantee acceptable performances and a durable second life cycle. For this reasons RJ cannot be considered as simple lubricants or viscosity regulators, which is an easy task. They also have the highly demanding task of restoring the original binder properties and performances. This includes resistance to rutting and fatigue cracking, which are somehow in contrast, since the first one requires high stiffness and elasticity, while the second one is favoured by the binder compliance. Moreover, the binder should resist to thermal cracking, low temperatures and so on. Therefore, an appropriate choice of the RJ should take into account the whole range of performances. However, those performances depend on the binder structure, which consists in a delicate colloidal equilibrium regulated by the relative quantities of bitumen constituents. In other words, the main task for the RJ can be seen as restoring, as much as possible, the original binder structure. The short-time aging is mainly associated to the loss of low molecular weight, more volatile, molecules that happens during laying and compaction of the pavement. This variation in the binder composition can be easily compensated with a new feeding of these components. In contrast, the long-time oxidative aging determines the appearance of new functional groups that alters the polarity of the molecules and thus their interactions and degree of aggregation with the other binder components. The long-term aged binder has a colloidal structure that can be profoundly changed with respect to the original one and the variation of the relative percentages of the so-called SARA (saturates, aromatics, resins, and asphaltenes) fractions makes almost impossible to re-obtain the virgin internal structure. The consequence is that a rejuvenated binder will never perform as it did in his first life. For this reason, it is necessary to investigate its properties in an as wide as possible way. From this point of view, the rheological approach is very helpful since in the linear viscoelastic range, the time temperature superposition principle allows estimating the material properties in an extremely wide frequency (temperature) range. Moreover, the calculation of the apparent molecular weight distributions is a valuable tool to estimate the above mentioned state of aggregation-interactions among molecules. This study is a first attempt to use this approach in the evaluation of the performances and durability of the rejuvenated binder.

Blends with different percentages of RJ were prepared and tested and a first indication that came out is that even the choice of the optimal percentage is ambiguous. Low percentage of RJ gave magnitude of the complex modulus and damage resistance comparable with that of the unaged binder. However, the phase angle master curve indicates that at low-medium reduced frequencies (high-medium temperatures) there is the need of a higher RJ quantity, but a higher RJ quantity may be a problem if it softens too much the binder at the operating temperatures. On the other side, the RJ is more prone to evaporation at the laying temperatures and this determines a different condition after RTFO. In other words, the partial evaporation of the RJ during compaction and laying may compensate the excess of oil necessary for a good workability and restore good performance properties. Finally, all the tests indicate that the rejuvenated binders have an aging susceptibility comparable with that of the original binder, irrespective of their RJ content.

References

Behnood A., 2019, Application of rejuvenators to improve the rheological and mechanical properties of asphalt binders and mixtures: A review, Journal of Cleaner Production, 231 171–182.

Cuciniello G., Filippi S., Cappello M., Leandri P., Polacco G., 2020, A revised relationship between molecular weight and reduced angular frequency in δ-method applied to unmodified petroleum bitumens, Road Materials and Pavement Design, DOI: 10.1080/14680629.2020.1828153

Petersen J.C., Glaser R., 2011, Asphalt Oxidation Mechanisms and the Role of Oxidation Products on Age Hardening Revisited, Road Materials and Pavement Design, 12, 795–819.

Sabouri M., Mirzaiyan D., Moniri A., 2018, Effectiveness of Linear Amplitude Sweep (LAS) asphalt binder test in predicting asphalt mixtures fatigue performance, Construction and Building Materials, 171, 281–290.

Themeli A., Chailleux E., Farcas F., Chazallon C., Migault B., 2015, Molecular weight distribution of asphaltic paving binders from phase-angle measurements, Road Materials and Pavement Design, 16, 228–244.

Yusoff Md., Monieur N.I.D., Airey A.G., 2010, The 2S2P1D: An Excellent Linear Viscoelastic Model, UNIMAS e-Journal of Civil Engineering, 1, 1–7.

Zhang X., Zhang K., Wu C., Liu K., Jiang K., 2020, Preparation of bio-oil and its application in asphalt modification and rejuvenation: A review of the properties, practical application and life cycle assessment, Construction and Building Materials, 262.