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Rejuvenating Agents vs. Fluxing Agents: Their Respective Mechanisms of Action on Bitumen Subjected to Multiple Aging Cycles

Abraham A. Abe [1], Paolino Caputo [1,*], Shahin Eskandarsefat [2,*], Valeria Loise [1], Michele Porto [1], Eugenia Giorno [1], Loretta Venturini [2] and Cesare Oliviero Rossi [1]

[1] Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 14/D, 87036 Rende, CS, Italy
[2] Iterchimica S.p.A., 24040 Suisio, BG, Italy
* Correspondence: paolino.caputo@unical.it (P.C.); shahin.eskandarsefat@iterchimica.it (S.E.)

Abstract: During the service life of road pavements, the asphalt, more specifically the surface layer, is susceptible to aging due to the oxidation phenomenon and the loss of the volatile compounds of bitumen, which functions as the binder in the asphalt conglomerate. Road pavements that undergo a significant level of oxidation become rigid and susceptible to cracking, and new paving operations will need to be carried out in order to make the road ideal for continued use. However, due to recent eco-friendly initiatives that have been put in place to promote a circular economy and also mitigate the problem of environmental pollution, the asphalt industry is currently devising means of safeguarding the environment while also minimizing the cost of the production of road pavements without compromising their quality. As a general solution to this issue, old asphalt pavements are removed and recycled as reclaimed asphalt (RA), with the aim of restoring the original properties of the binder in such a way that RA can be re-used in combination with virgin materials to produce new road pavements. In this research study, virgin bitumen is subjected to a cycle of aging, after which two recycling agents are used to modify the aged bitumen samples. These samples containing the different recycling agents were subjected to a second aging cycle, a second recycling agent treatment, and then again subjected to a final aging cycle. The two recycling agents have different compositions, and each one of them could be either a rejuvenating agent or a fluxing agent. This study investigates the effect of these recycling agents on aged bitumen, and how the addition of these recycling agents influences the changes observed between virgin, aged and recycled bitumen. This would enable an understanding of rejuvenation and fluxing mechanisms, which will help in the classification of the asphalt recycling agents as either rejuvenating or fluxing agents. Dynamic shear rheology, atomic force microscopy, and light microscopy to determine asphaltene melting point were the techniques used in this investigation. The results obtained demonstrate that rejuvenating agents are more effective in reversing the effects of oxidative aging on the bitumen binder than fluxing agents.

Keywords: recycling agents; rejuvenating agent; fluxing (softening) agent

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1. Introduction

Carbon reduction commitments after the UN Climate Change Conference (COP26) 2021 and Paris summit have sensitized governments on the environmental concerns more than ever. As one of the main carbon-affiliated sectors, within the road industry, several technologies have been proposed to reduce the carbon equivalent of asphalt pavement construction and maintenance interventions [1,2]. None of these technologies and initiatives is more practical and generally accepted in the road industry than the recycling of reclaimed asphalt (RA). Although, in terms of material functionality, recycling RA has been improved over the past few decades, several limitations still remain. For instance, it has been shown that when RA is incorporated in a high ratio in an asphalt mix, producing quality recycled asphalt is dependent on the correct choice of the type, dosage, and application method of the recycling agent [3].

To date, many different design flowcharts or blending charts have been proposed to optimize the dosage of the recycling agents, mostly considering only the physical properties determined by conventional binder tests, i.e., viscosity, penetration, softening point, etc. However, recent research shows that the mechanism of a complete rejuvenation is not a unilateral but a multilateral action [4]. Different recycling agents have unique and varying potential to address the deficiencies of aged binders to different extents [5,6]. In other words, it can be said that all of the additives that are being used for recycling purposes could be considered as recycling agents; however, not all of them are rejuvenating agents. To investigate the multilateral mechanism of recycling, in addition to physical and mechanical properties characterization, which is usually the primary step, several techniques have been introduced in research and practice. These can be divided into microscopic, physico-chemical, and chemical techniques, and so on. Among these techniques, microscopic analysis, such as atomic force microscopy (AFM), that provides knowledge on the microstructural properties is a widely popular approach. Regardless of what the different features in AFM images correlate to, there is a consensus on the fact that while some recycling agents damage the chemical morphology of aged bitumen, there are some others that could restore it [2,7]. This restoration could be achieved either by dispersing the so-called bee structures and reducing their size, or regenerating the dominant para phase [8,9]. This may or may not be observable during conventional bitumen tests [10,11]. Compared to AFM, light microscopy has been less applied in this context. This is due to the technical inadequacy of light microscopy for bitumen observation purposes. However, the authors have successfully used this technique in previous studies to investigate asphaltene thermal properties, including melting point. The technique is based on the fact that during the oxidation of bitumen, the asphaltene clusters tend to increase in size and texture, as explained by the Yen–Mullins model. Based on the results, while the addition of one of the recycling agents reduced the melting point of the asphaltenes to values close to the reference value, the others did not [12].

In the investigation of the chemical composition of virgin and aged bitumen, SARA analysis is a technique frequently used for investigating recycling agents and differentiating rejuvenators from those of flux oils (softeners). A real bitumen rejuvenation mechanism involves the rejuvenator influencing changes in the colloidal matrix of aged bitumen, which restores the asphaltene–maltene ratio to a state similar to that of virgin bitumen [13]. Recycling agents, especially fluxing oils, may reduce the viscosity and modulus of the overall bitumen through lowering the viscosity of the continuous solvent phase, but may have little effect on the intermolecular agglomeration and self-assembly of the polar micelles [14]. Despite the sensitivity of the method, it has been recognized as a valid approach for investigating bitumen aging in general [2,5,9].

2. Materials and Methods

2.1. Materials

For the purpose of this study, a 70/100 paving grade bitumen was used. Table 1 represents some of the given physical properties of the bitumen. The additives were two recycling agents in liquid form, and for the purposes of this study were called R1 and R2. Table 2 summarizes some of the properties of the recycling agents. The additives were added in a proportion of 6% to the aged samples (by weight of bitumen). It is worth mentioning that the choice of the dosage was based on the preliminary stages of this research [3,9], where different dosages were investigated, and 6% was found as the optimum dosage for the recycling agents.

Table 1. Some of the given characteristics of the base virgin 70/100 bitumen.

Characteristic	Unit	Value	Method
Penetration @25 °C	dmm	70–100	EN 1426:2015
Softening point	°C	43–51	EN 1427:2015
Dynamic viscosity @135 °C	Pa.s	≥0.23	EN 13702:2018
Flash point	°C	Min 250	EN ISO 2592:2017
Fraass breaking point	°C	Max −10	EN 12593:2015

Table 2. Some of the given properties of the recycling agents.

Characteristic	Unit	Recycling Agent 1 (R1)	Recycling Agent 2 (R2)
Aspect	-	Liquid	Liquid
Color	-	Yellow	Yellow
Viscosity	cP	25–50	20–30
Pour point	°C	≤−5	≤0
Chemical nature	-	Mix of amino derivatives	Blend of vegetable esters

2.2. Sample Preparation

In order to add the recycling agents to the aged bitumen sample, the bitumen was first heated to a temperature of 150 ± 5 °C. The recycling agent was then added and mixed with the bitumen using a high-speed shear mixer set to 500–700 rpm in order to obtain a homogenous mixture. It should be noted that although for the first round of the aging, both short-term and long-term aging were applied by means of a rolling thin film oven (RTFO) and pressure aging vessel (PAV), respectively, in the second round, the samples were only subjected to PAV aging. Multiple PAV aging was conducted in order to strongly oxidize the bitumen and simulate real-life duress to which asphalt pavements are normally subjected. Based on the consecutive steps listed below, the performances of the recycling agents were evaluated by testing the samples using techniques explained further in each specific section. The testing plan and applied ID for the samples are shown in Table 3 as follows.

Table 3. Testing steps and the corresponding samples.

Testing Step	Testing Bitumen
1	Virgin bitumen
2	RTFO + PAV bitumen
3	(RTFO + PAV bitumen) + R_i
4	(RTFO + PAV bitumen + R_i) + PAV
5	(RTFO + PAV bitumen + R_i + PAV) + R_i
6	(RTFO + PAV bitumen + R_i + PAV + R_i) + PAV

R_i refers to recycling agent 1 and 2.

2.3. Asphaltene Extraction (Deasphaltenization)

The asphaltenes were extracted from bitumen by exploiting their differential solubility. The protocol carried out has also been used for a previous study [12], and is a slight modification of ASTM standard protocol D2007-80 of asphaltene extraction [15]. A specific amount of bitumen was weighed into a tube and then dissolved in equal part chloroform, i.e., 1 g of bitumen in 1 mL of CCl_4. Upon complete dissolution of the bitumen in the solvent, 40 times its volume of n-pentane was added and the tube was vortexed to homogenize the solution. The asphaltenes started to precipitate in the solution because n-pentane is a differential solvent of bitumen. The tube was sealed with a stopper and parafilm and kept in a dark chamber for 24 h. The solution was then filtered using a pre-weighed Whatman 1002-090 filter paper with a diameter and pore size of 90 mm and 8 μm, respectively. The asphaltenes remained on the filter paper, which was then placed in the oven at 60 °C for 2 h in order to allow evaporation of the n-pentane solvent. The filter paper was then weighed again to determine the percentage of asphaltenes obtained from the specific quantity of bitumen weighed as this percentage varies from one bitumen to another. The asphaltenes were then collected and analyzed. The whole deasphaltenization process was carried out at room temperature.

2.4. Rheological Analysis

Dynamic shear rheological analysis was carried out on the samples using a dynamic shear rheometer (SR-5000, Rheometric Scientific, Piscataway, NJ, USA) equipped with a parallel plate geometry with a diameter of 25 mm. The mechanical properties of bitumen were measured by carrying out a temperature sweep (TS), commonly known as a time cure test. This involves subjecting the bitumen sample to slowly increasing temperatures until the bitumen loses its elastic modulus and only its viscous modulus remains. This was conducted to determine the transition temperature of bitumen. This transition temperature is the temperature at which bitumen transitions from viscoelastic solid to viscoelastic non-Newtonian fluid [16]. The time cure test was performed using the following parameters:

- Temperature, 25–120 °C (increasing at the rate of 1 °C per min).
- Stress, 100 Pa.
- Parallel plate geometry, 25 mm diameter with a 2 mm gap.
- Frequency, 1 Hz.

2.5. Atomic Force Microscopy

Atomic force microscopy (AFM) studies were carried out using a Bruker Nanoscope VIII microscope set to tapping mode. The oscillations of the cantilever were regulated close to its resonance frequency of 150 kHz. As a result of the upwards and downwards oscillation of the cantilever, its tip interacts sporadically with the surface of the sample. This interaction between the sample surface and the cantilever tip brings about the vibration of the cantilever. The morphological features of the tested sample determine the magnitude of the vibrations, which is influenced by the phase angle shift of the of the cantilever tip when it vibrates, signifying energy dissipation in the tip–sample ensemble. Cantilevers with elastic constants of 5 N/m and 42 N/m were used for the measurements. Phase and topography images were taken contemporarily.

2.6. Light Microscopy to Determine Asphaltene Melting Point

Light microscopy of asphaltenes was carried out using a Prior Scientific Instruments MP3500K light microscope equipped with a Canon EOS 4000D camera to capture real-time images under the microscope. This microscope setup was coupled with a Eurotherm 246 temperature regulator connected to a heating panel placed on the stage of the microscope. The extracted asphaltene samples were placed in a double microscope glass slide (sandwich model), and then the glass slide was placed on the heating panel on the stage of the microscope. A temperature ramp was applied with a starting temperature of 120 °C and a heating rate of 5 °C per minute. For every 5 °C increase in temperature, the samples were exposed for 1–2 min to ensure uniformity and homogenous heating through the sample. The glass slide containing the asphaltenes was observed under the microscope at a magnification of 20×, and images were captured in real time.

3. Results and Discussion

3.1. Rheological Properties

In the first stage of this research, as an essential procedure, the effectiveness of the recycling agents in recovering the changed physical/rheological properties of the aged bitumen was assessed by means of conventional bitumen testing methods. According to the results, which are summarized in the Table 4, as expected, every cycle of aging increased the stiffness of the bitumen, and each recycling action brought about the recovery of the mechanical properties of the aged bitumen. Based on the results, it can also be inferred that all of the tested recycling agents were capable of recovering the fundamental physical properties of the aged bitumen, and no significant difference was recorded between the obtained results. In other words, at this stage, both recycling agents could be classified as fluxing (softening) agents.

Table 4. The physical/rheological properties of test bitumen with and without the recycling agents.

Sample	Penetration (dmm)	Softening Point (°C)	Dynamic Viscosity (Pa·s)	
ID	25 °C	-	100 °C	135 °C
Virgin bitumen	76	44.8	11.4	1.2
RTFO + PAV Bitumen	51	57.5	38.8	2.6
(RTFO + PAV Bitumen) × 2nd PAV	38	66.5	68.5	4.0
(RTFO + PAV Bitumen) × 3rd PAV	28	75.8	141.6	5.7
(RTFO + PAV Bitumen) + R1	74	46.0	-	-
(RTFO + PAV Bitumen) + R2	75	44.2	6.4	0.8
(RTFO + PAV Bitumen + R1) + PAV	70	52.8	-	-
(RTFO + PAV Bitumen + R2) + PAV	74	44.6	-	-
(RTFO + PAV Bitumen + R1 + PAV) + R1	72	43.3	-	-
(RTFO + PAV Bitumen + R2 + PAV) + R2	80	41.8	8.0	0.8
(RTFO + PAV Bitumen + R1 + PAV + R1) + PAV	78	41.4	7.3	0.8
(RTFO + PAV Bitumen + R2 + PAV + R2) + PAV	68	52.6	11.5	1.1

Bitumen, upon aging, becomes stiffer and more rigid, thereby increasing its transition temperature. In this study, from the rheological point of view, the complex modulus G* which is bitumen's overall resistance to deformation is evaluated in relation to the loss tangent (tan delta). Tan delta is the relationship between the storage (viscous) modulus (G″) and the loss (elastic) modulus (G′) of the material. G* is a direct measure of the rigidity of bitumen's soft solid structure when exposed to stresses below the yield stress, and this makes it a good indicator of the flexibility or stiffness of bitumen. With increasing temperature, G′ decreases at a faster rate than G″, and so a crossover temperature occurs. This temperature is the temperature that was earlier referred to as the transition temperature [17]. The DSR profiles shown below depict G* in relation to the crossover temperatures of the samples. Higher transition temperature values imply greater stiffness of a sample.

The reference samples for this study were virgin bitumen and three other samples that were subjected to multiple aging. This, on one hand, was conducted in order to simulate the realistic multiple aging cycles, and, on the other hand, to compare them to the samples containing recycling agents that were also aged multiple times. As can be seen in Figure 1, with each increasing aging cycle, the transition temperature, which corresponds to the loss tangent, increases significantly.

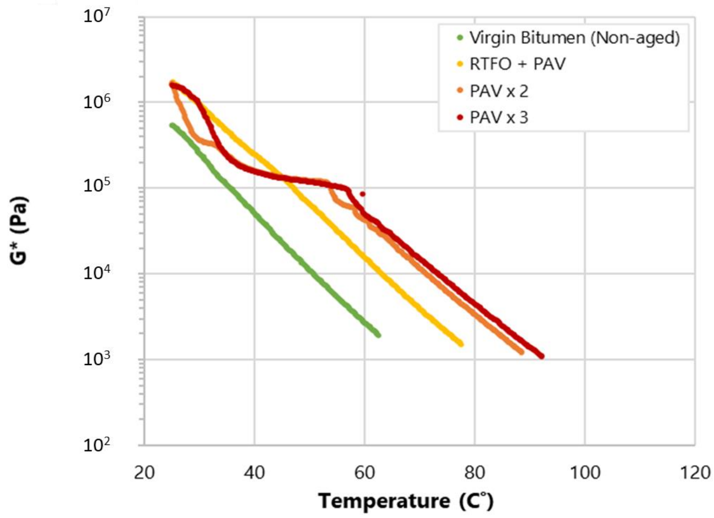

Figure 1. Complex modulus G* vs. temperature of reference samples.

Figure 2 shows that both recycling agents are effective, and were able to recover the physical properties by reducing the stiffness of the aged binder. It is interesting to note that R1 even after two aging cycles was able to restore the bitumen almost exactly to its initial unaged state. The R1-modified sample remained the same even after another subsequent final aging cycle. According to Figure 2, R2 was also able to reduce the stiffness of the aged bitumen, even though it did not do this as effectively as R1. It is also important to observe that the sample that was recycled with a second dose of R2 became softer than the virgin bitumen, whereas the corresponding R1 sample was strikingly similar to the virgin bitumen when also considering the transition temperature. This suggests that R1 has a higher effective recycling potential compared with the R2 recycling agent due to the high effectiveness and specificity of the R1 recycling agent in recovering the aged bitumen samples' original properties. This rheological analysis is very useful and indicative of the mechanical properties of the bitumen binder, but it may not be enough to distinguish a rejuvenating from a fluxing effect of recycling agents.

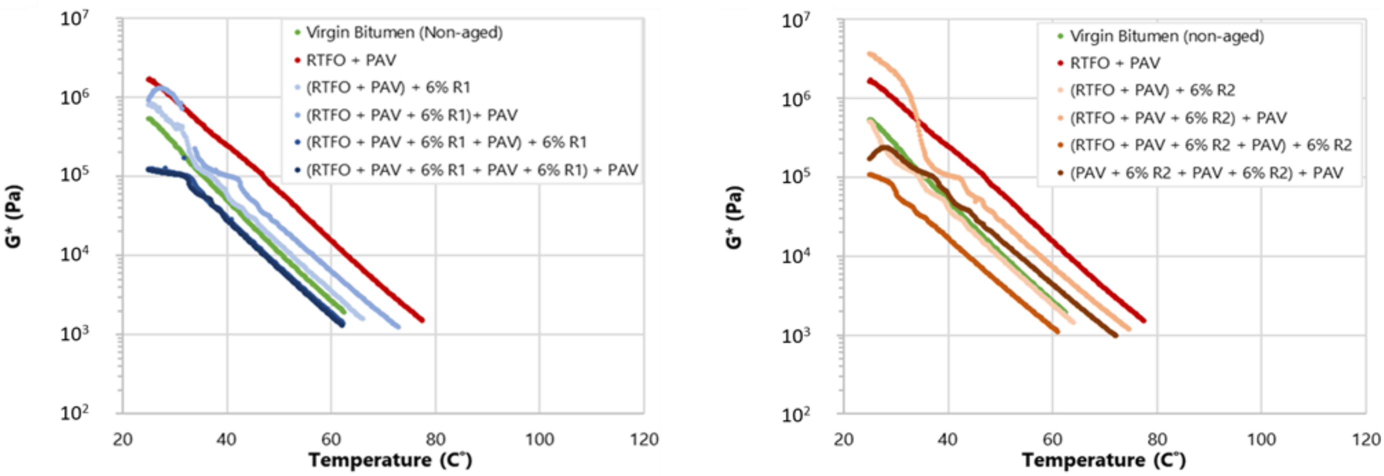

Figure 2. Complex modulus G* vs. temperature of R1- and R2-modified samples.

3.2. Morphological Properties

Within the existing literature, AFM has been found to be a useful technique that can be used to study bitumen's inner structure as it allows the topographic characterization of surfaces at resolutions not available with light microscopy. It is also more practical and straightforward than scanning electron microscopy (SEM) because AFM samples require minimal preparation. Using the AFM technique for the purpose of studying bitumen's inner structure, four phases are usually observed in the images: catana phase (consisting of bee structure), peri phase, para phase, and sal phase [2].

i. The catana phase is made up of so-called bee structures, which resemble undulated wavy structures having a morphology of alternating swellings and depressions.
ii. The peri phase is the domain surrounding the bee structures.
iii. The para phase is dominant in bitumen's matrix, flat in nature, and surrounds the peri phase.
iv. The sal phase in combination with the para phase consists of aromatics and saturates, and these constitute the smooth matrix.

Evidence from a literature review of AFM studies carried out on bitumen suggests that several interpretations of AFM images exist among researchers. The bee structures are speculated to be connected to bitumen's asphaltenic composition, with resins being the regions surrounding the bee structures. Aromatics and saturates are said to correspond to the smooth matrix (para and sal phases) observed in AFM images [18–21]. Regardless of differences in opinion regarding interpretation, AFM studies provide a wealth of useful information, and are instrumental in understanding the intricacies of bitumen's inner structure.

As can be seen from Figure 3, the aging of the bitumen brought about an enlargement and roughening of the catana phase. This can be explained by the incorporation of oxygen by the asphaltenes during aging, and this translates to an increase in stiffness and rigidity of the bitumen, since the bee structures grow larger in size [22]. The para phase, which probably represents the maltenic fraction of bitumen, also diminished with aging. The addition of the R1 recycling agent is shown to reduce the size of the asphaltenes, and also restore the maltenic fraction, thus making it similar to non-aged bitumen. These aforementioned changes in bitumen's morphology were repeatedly observed with the subsequent aging and addition of R1 recycling agent. The bee structures increased in size due to their incorporation of oxides via oxidative aging, and also formed clusters. These clusters usually occur due to asphaltene aggregation, making the aged bitumen stiff and fragile, and thus susceptible to cracking [23]. The first addition of the R1 recycling agent reversed this increase in bee structure size, and then the second aging cycle increased the bee structure size again. The second cycle of R1 modification of the aged bitumen brought about, once again, a reduction in the size of the bee structures; the third aging cycle slightly increased the bee structure size, even though the effect of the third cycle of aging on the recycled bitumen was not highly pronounced, likely due to the significant amount of the R1 recycling agent present in the sample. This shows the effectiveness of R1 in restoring the balance of the ratio of the different fractions of aged bitumen, reversing the effects of multiple aging cycles.

In Figure 4, on the other hand, it can be observed that upon the first addition of the R2 recycling agent to the aged bitumen, the agglomeration of bee structures observed in the aged sample was de-clustered in such a way that a few clusters still exist, but these small clusters seem to be dissolved clusters resulting from a larger cluster. When this recycled sample was aged for the second time, the peri phase surrounding the de-clustered bee structures became more pronounced. This indicates an augmentation of the peri phase, which was most likely brought about by the first addition of the recycling agent. Since the peri, para, and sal phases are more related to the maltenic fraction of bitumen [24–28], it is very likely that R2 functions to augment the maltenic fraction of aged bitumen. The second addition of the R2 recycling agent shows a further dilution of the bee structures in the smooth matrix, as they are more separated but less abundant in the aged bitumen's matrix. The third aging cycle shows a few bee structures dispersed in the smooth sal phase, indicating a mere fluxing and softening of the bitumen rather than real rejuvenation, as observed in the case of the R1 recycling agent. The addition of the R2 recycling agent significantly augments the maltenic fraction (para phase). The asphaltenes maintain the size they gained after aging, and are dispersed in an abundant maltenic matrix.

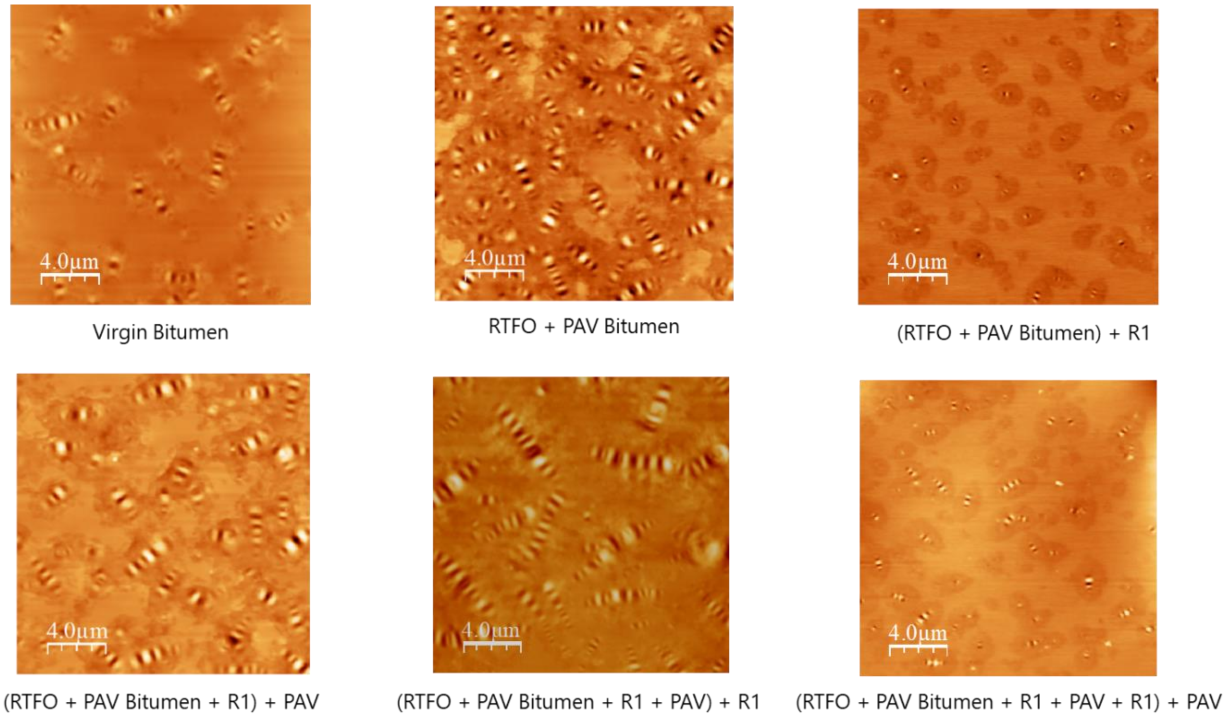

Figure 3. AFM images of virgin, aged, and R1-modified samples.

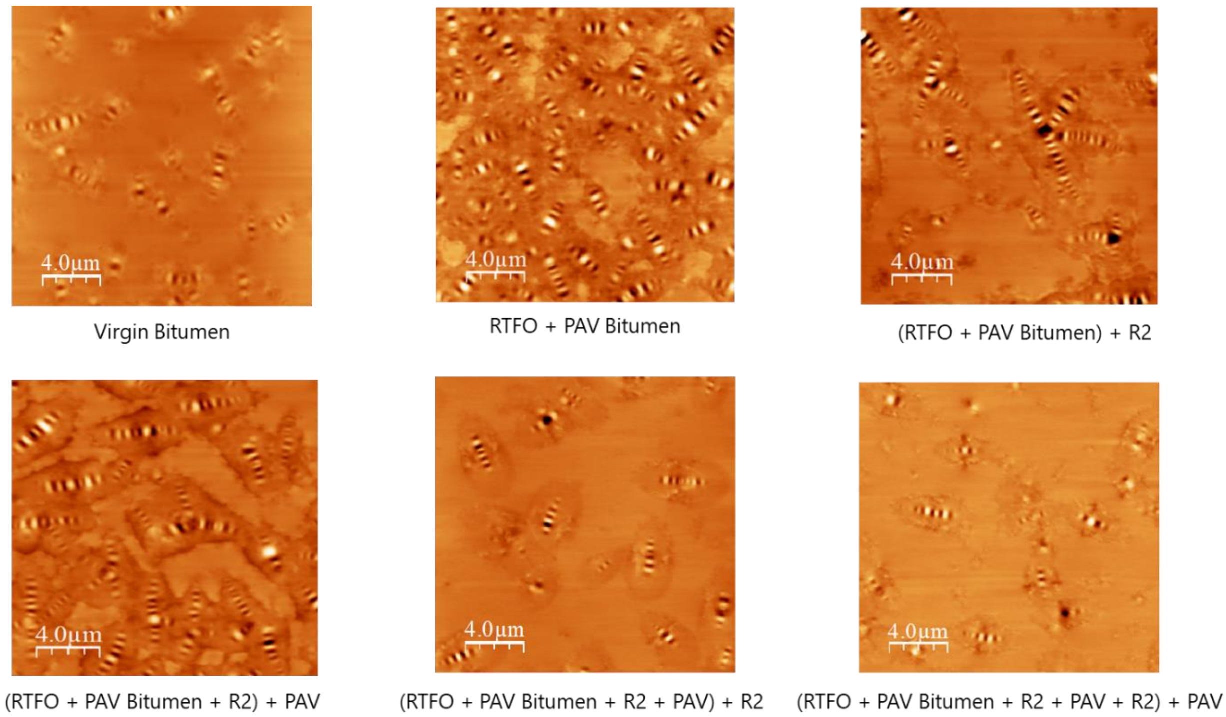

Figure 4. AFM images of virgin, aged, and R2-modified samples.

In the virgin bitumen sample, the bee structures (catana phase) surrounded by the peri phase are distinctly positioned, showing that they are dispersed in the para phase. Oxidative aging disrupts this colloidal system and causes an increase in size coupled with a clumping together of the bee structures [29]. Technically, a rejuvenator should work by restoring the morphological structure of the aged bitumen to that described for virgin bitumen. Instead, a fluxing/softening agent functions as an oil, and thus interacts with the peri, para, and sal phases, leaving the bee structure morphology unchanged in the colloidal matrix. Based on the information provided by AFM analysis, the R1 recycling agent could interact with bitumen's components on a chemical level, reversing the effects of oxidative aging, thus rejuvenating the aged bitumen. The R2 recycling agent, on the other hand, could only augment the maltenic fraction, and did not significantly interact with the bee structures or their morphology. This could mean that it merely fluxes the bitumen by reducing its viscosity.

3.3. Light Microscopy to Determine Asphaltene Melting Point

This is a microscopy technique that also combines the use of a light microscope with the concept of basic calorimetry. It involves monitoring the response of asphaltene particles to a gradual increase in temperature, and this response can be observed in real time under the microscope. Even though this technique is a qualitative method, its validity and accuracy has been verified using differential scanning calorimetry, as shown in previous studies [2,12,17]. This microscopy technique is a form of real-time observation of the transition from one state to another, a parameter that differential scanning calorimetry usually measures. Bitumen, after aging, exhibits an increase in rigidity in its solid form and viscosity in its liquid form. Since the asphaltenes are the fraction of bitumen susceptible to oxidative aging [22,27], it is only logical to investigate the response of asphaltenes to an increase in temperature. Aged asphaltenes become more heat resistant, and melt at higher temperatures compared to unaged virgin bitumen [23,29]. The melting point of an asphaltene is the temperature at which it transitions from a crystalline to an amorphous state. The images in Figure 5 show the asphaltenes of each sample and the temperatures at which they transition from crystalline to amorphous states.

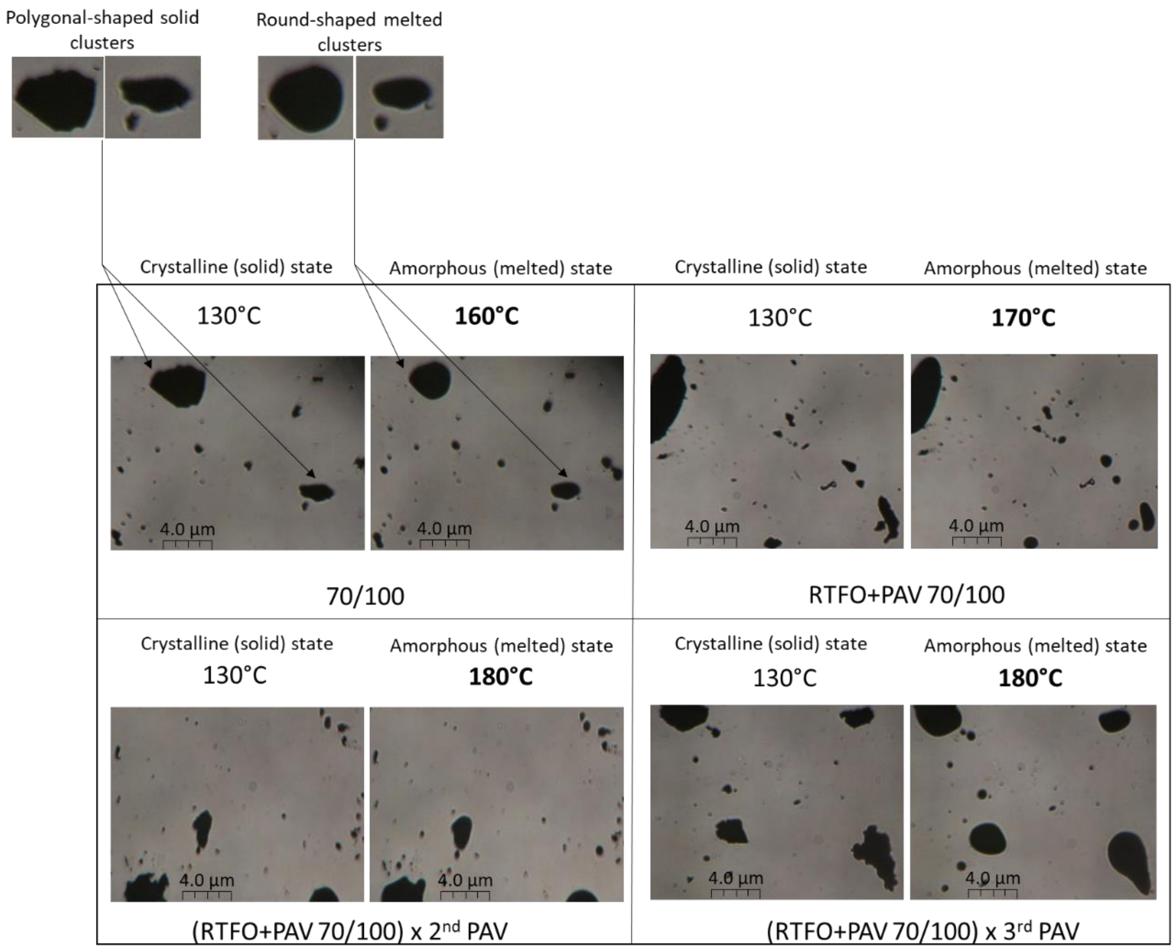

Figure 5. Light microscopy images indicating asphaltene melting points of virgin and aged 70/100 bitumen.

In Figure 5, it can be observed that with each cycle of aging, the melting point of the asphaltenes of the virgin bitumen continues to increase. The highest melting point was observed in the sample that underwent three PAV aging cycles. Upon the addition of the R1 recycling agent to the bitumen that was aged once, it can be observed from Figure 6 that the melting point of the asphaltenes of the recycled bitumen reduced from 170 °C to 155 °C, which is 5 °C lower than the virgin bitumen. This shows the capacity of the R1 recycling agent to restore the thermal properties of the asphaltenes of aged bitumen. Upon the aging of this recycled sample, the melting point of the asphaltenes increased, this time to 165 °C, which is 5 °C higher than the melting point of the virgin bitumen asphaltene sample. This aged bitumen was modified again with the R1 recycling agent, and the melting point decreased to 160 °C (the same melting point as the virgin bitumen asphaltene sample). A final aging cycle was carried out on the twice-recycled bitumen, and it was observed that the asphaltene melting point increased once again to 165 °C. This could mean that the R1 recycling agent is capable of interacting chemically with the asphaltenes of the aged bitumen, thereby restoring their properties that were lost due to oxidative aging.

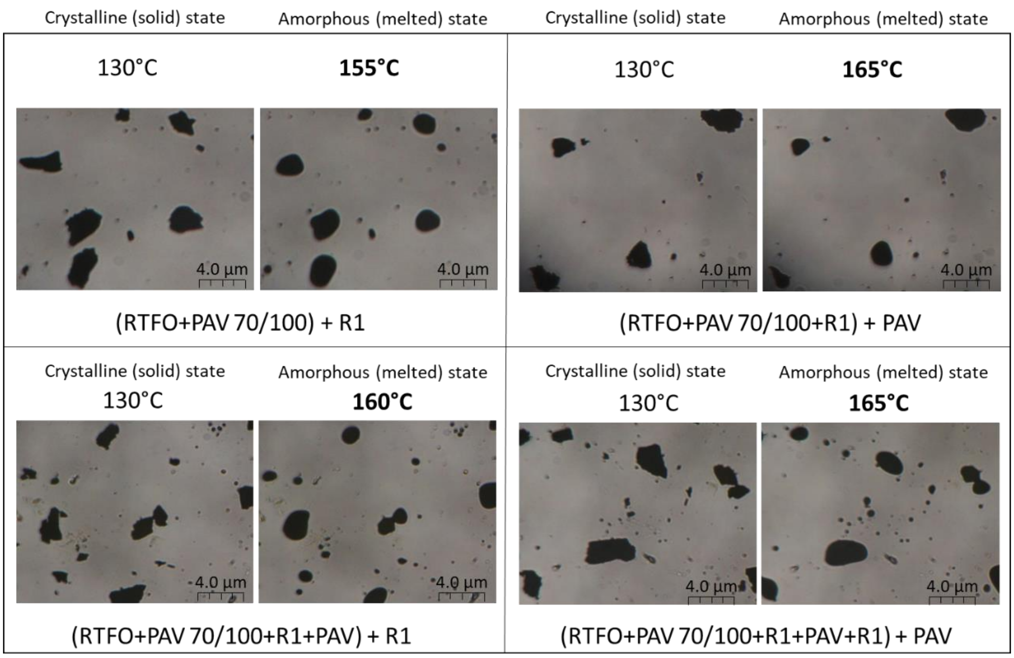

Figure 6. Light microscopy images indicating asphaltene melting points of R1-modified and aged 70/100 bitumen.

On the other hand, in the case of the R2 recycling agent, when it was added to the bitumen sample that was aged once, the melting point of the asphaltenes reduced from 170 °C to 160 °C, as can be seen in Figure 7. This recycled sample was aged again, and the melting point of the asphaltenes increased to 165 °C. This twice-aged sample was modified again with R2, and the melting point of the asphaltenes was even higher (180 °C, which is the same melting point as the neat bitumen aged twice). This means that the second modification of the bitumen with the R2 recycling agent was not effective, and even worsened the effects of aging on the asphaltenes thermal properties. This twice-recycled bitumen was aged for the third time, and the asphaltene melting point remained the same at 180 °C. It can thus be said that the R2 recycling agent, after the first recycling process, did not in any way improve the bitumen sample. This could be because R2 is a mere fluxing agent that softens the bitumen and reduces its viscosity. It does not truly interact chemically with the aged bitumen to restore its virgin properties. Fluxing agents only augment the maltenic fraction of bitumen, thus reducing its viscosity and improving its flow. No real changes in the chemical structure of aged bitumen are usually observed when a fluxing agent is used to modify bitumen [2,17].

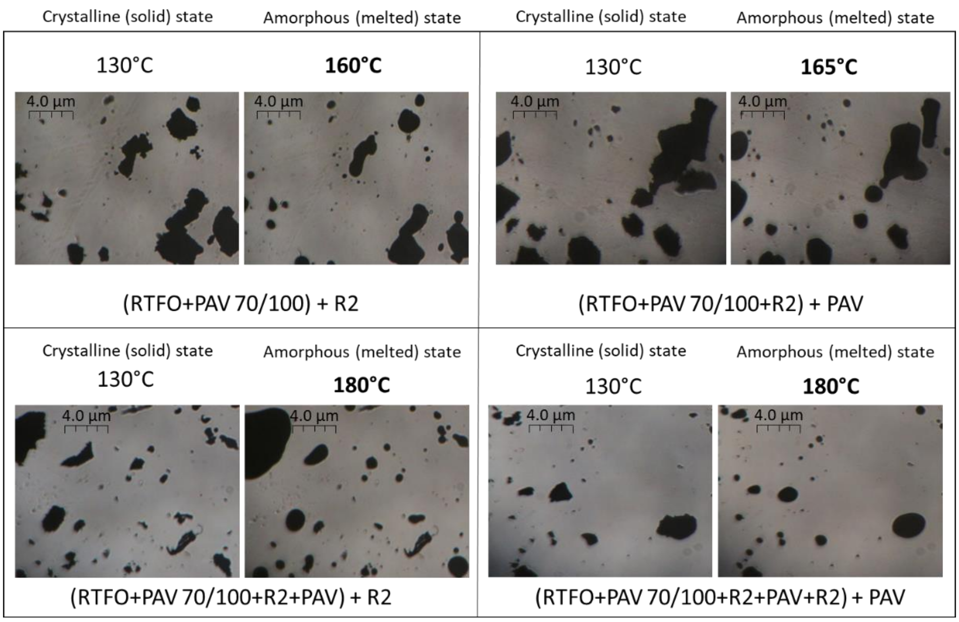

Figure 7. Light microscopy images indicating asphaltene melting points of R2-modified and aged 70/100 bitumen.

The melting point values for each sample are reported in Figure 8, which shows a histogram with the asphaltene melting point temperatures of all the bitumen samples investigated in this study. In general, this simple microscopy technique was found to be instrumental in distinguishing a rejuvenating from a mere fluxing effect.

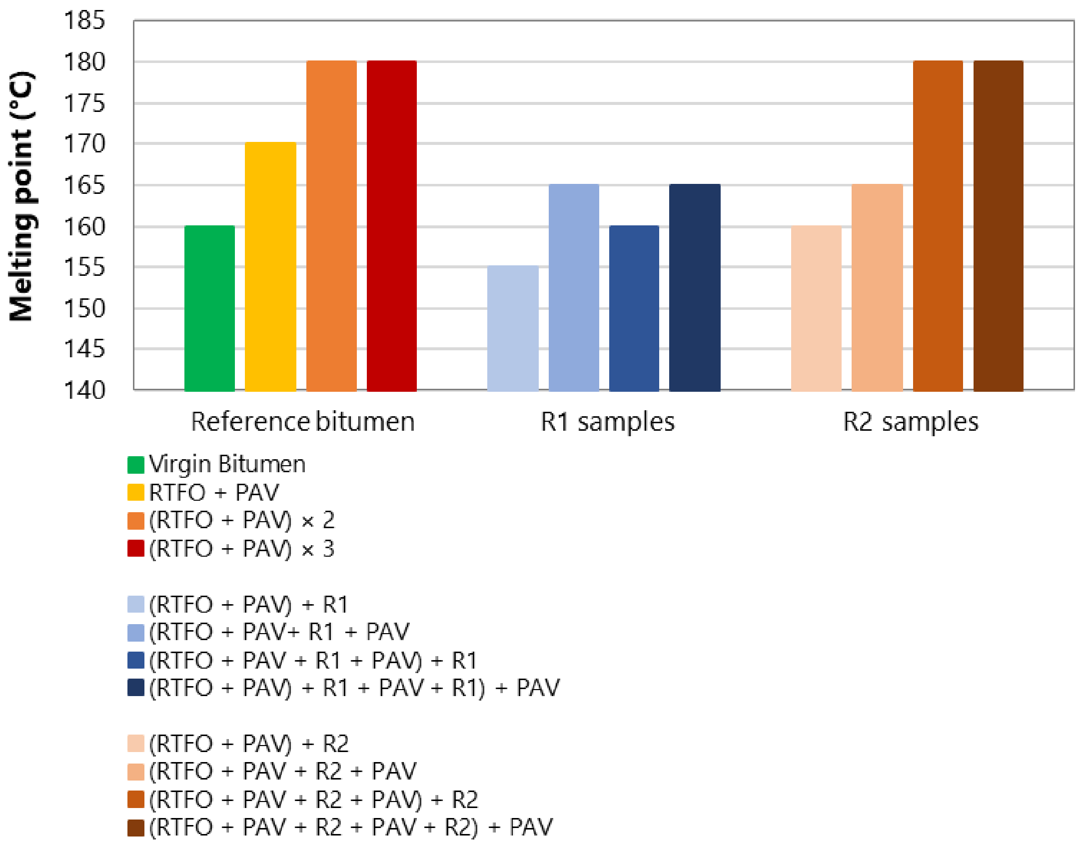

Figure 8. Melting point values of the asphaltenes extracted from each sample.

3.4. Rejuvenating Effect vs. Fluxing Effect: Action Mechanism of Recycling Agents

Generally speaking, this study shows how differently the two recycling agents function. The techniques applied in this study are able to provide indications on the effects of these recycling agents on aged bitumen, thereby enabling the characterization of their mechanisms of action. A real rejuvenator is capable of restoring the chemical compounds that were lost during aging, and also of breaking down the oxides formed with the hydrocarbons and sulfides that make up bitumen's composition [30–34]. The R1 recycling agent, which the results suggest is a real rejuvenator, is made up of a blend of compounds composed of amino groups, as can be seen in Table 2. It is very plausible that the amino derivatives interact with the part of the bitumen that was oxidized (the asphaltenes), thereby reconstructing their chemical structure and reversing the asphaltene aggregation phenomenon that brings about stiffness of aged bitumen. Asphaltenes are known to consist of condensed aromatic rings and heterocyclic compounds that contain nitrogen and sulfur, and oxidative aging depletes these compounds and also triggers the formation of oxides such as sulfoxides, which have been identified in aged bitumen [17]. The reconstruction of the chemical structure of aged bitumen by the R1 recycling agent could be as a result of the fact that amine groups, in general, consist of five-membered heterocyclic rings that contain nitrogen, and these compounds could either replace the depleted compounds in aged bitumen or supplement the existing ones, while also breaking down the dative bonds of the sulfoxide groups that are characteristically present in high quantities in aged bitumen. The R2 recycling agent, on the other hand, is a mix of plant esters. Given that the findings of this study suggest that R2 is not capable of interacting chemically with aged bitumen, but rather establishes a physical interaction by augmenting the maltenic fraction, it can be said that it is a mere fluxing agent. The R2 recycling agent is composed of plant esters; these also contain heterocyclic rings, but are predominantly composed of carboxylic acids, heterocyclic rings, and alcohol. Esters are also well known to function as excellent lubricants, and, in this case, it can be said that the action of R2 on oxidized bitumen is the dilution of oxidized asphaltenes and not real rejuvenation via the regeneration of heterocyclic or aromatic rings. This mechanism of action of the R2 recycling agent is not sufficient for the real rejuvenation of aged bitumen, and this could explain why R1 made up of amino derivatives is a better candidate at restoring the structural properties of aged bitumen compared to R2, which is made up of plant esters. Asphaltene aggregation is also characteristic of aged bitumen, and this is brought about by the interaction between the polyaromatic cores of the asphaltene molecules. Van de Waal forces between the aliphatic side chains of the asphaltene molecules also contribute to this aggregation and clustering [35,36]. Since the AFM images show the de-clustering of the bee structures brought about by R1 in aged bitumen, it is possible that the tendency of alkyl groups to surround N atoms in amino group molecules increases the steric interference between the asphaltene molecules, thus destabilizing the asphaltene clusters in aged bitumen [22]. The esters that constitute the R2 recycling agent are less likely to influence steric interference, and more likely to promote van der Waal forces between asphaltene molecules that sustain asphaltene aggregation [35]. These properties indicate why R1 seems to be an ideal rejuvenator and R2 seems to be a softener of aged bitumen, as shown by the results of this study.

4. Conclusions

In this study, two recycling agents were studied to investigate their rejuvenating capabilities on bitumen binders subjected to multiple aging cycles. Rejuvenating agents and fluxing agents have different mechanisms of action on aged bitumen. A rejuvenator should be able to interact chemically with the components of bitumen to restore its properties. It should be also able to recover its physical rheological properties to guarantee the long-term performance of a recycled asphalt mixture. A fluxing agent is capable of only physically interacting with the aged bitumen by augmenting its maltenic fraction, thereby making it softer. Studies that distinguish between real rejuvenation and mere fluxing of aged bitumen will prove to be very important in the advancement of RAP technology. These studies could highlight pathways that will bring about an increase in the percentage of reclaimed asphalt that can be used in new road paving operations and, in the long run, facilitate recycling and resource conservation, thereby promoting a circular economy.

The DSR, AFM, and optical microscopy findings of this study can be concluded thus:

- Dynamic shear rheology is fundamental in evaluating the mechanical properties of bitumen, and it often corroborates the results obtained from bitumen conventional tests. In fact, in this research, the conventional test results were also consistent with those of the DSR analysis. However, other techniques such as atomic force microscopy and light microscopy are very important in order to understand the mechanisms that govern the changes in bitumen's properties upon aging, and the recycling of bitumen with rejuvenators or mere fluxing agents.
- The DSR results show that both recycling agents used in this study reduced the stiffness of the aged bitumen, recovering its mechanical properties close to that of the reference virgin bitumen. This was observed via both complex modulus and the transition temperatures. As mentioned earlier, these results are consistent with those obtained from the conventional bitumen tests, as expected.
- Via AFM, the R1 recycling agent was observed to restore the internal structural components of the aged bitumen, bringing it back to a structure very similar to the reference virgin bitumen. R2 recycling agent was only able to augment the maltenic fraction of the aged bitumen, merely softening it.
- Via deasphaltenization and light microscopy of asphaltenes, it is observed that R1 effectively recovered the properties of the corresponding bitumen by restoring its property of change of state in relation to temperature. This was not observed with R2, meaning that it has little to no effect on the asphaltenes of aged bitumen. Since aging is said to have a major effect on the properties of asphaltenes, it can be said that R2, in the real sense, does not reverse the effects of oxidation.
- Adding up the test results of this study and comparing their implications with what is written in the scientific literature on this topic, recycling agent R1 can be said to be a rejuvenator, while recycling agent R2 can be said to be a fluxing/softening agent. Accordingly, the introduced methods could be efficient techniques to differentiate the recycling agents into fluxing (softening) agents and rejuvenators.

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