

Physicochemical interactions of reactive surfactants with bitumen

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Abstract

The use of reclaimed asphalt pavements (RAP) is gaining popularity in Europe, especially in the reconstruction of asphalt pavements. This fact has encouraged the seeking of modifying agents (rejuvenators and/or softeners) able to soften aged bitumen to optimise the reuse of RAP. Here, a set of reactive surfactants have been evaluated in terms of the effect caused on bitumen properties after modification. The selected reactive surfactants (dodecanyl succinic anhydride, DSA, and dodecylbenzenesulfonic acid, DBSA) consist of an aliphatic tail of 12 carbons in length and a polar head that contains a reactive group able to react with polar bitumen molecules. Blends of bitumen with 3 wt% additive have been prepared and analysed by means of rheological, thermal and analytical techniques. The obtained results point out that the addition of DSA reduces the stiffness and the viscosity of a model bitumen in the whole in-service temperature range, being more effective than a selected benchmark: engine oil. By contrast, the use of DBSA gives rise to an opposite effect, especially in the intermediate-high temperature range, where a remarkable increase of elastic and viscous properties is noticed. In general, the resulting data evidence the existence of chemical interactions of the reactive group of surfactants with polar compounds in bitumen that affect the colloidal stability. The different outcomes obtained seem to be caused by the nature of the new chemical bonds: ion pairs for DBSA and covalent links for DSA. **Keywords:** Physicochemical rejuvenation, viscoelasticity, reactive surfactants.

1. INTRODUCTION

Traditionally, the modification of bitumen properties has been performed by means of passive polymers (physically mixed with bitumen, e.g. thermoplastics elastomers, plastomers, crumb tyre rubber), active or reactive polymers (e.g. polymer containing reactive groups: anhydride, isocyanate, epoxide, etc.) and other non-polymeric reactive agents (e.g. acids, organic molecules, dioxide/thiourea-derivatives, etc.) [1, 2].

However, as a consequence of the high mixing temperatures involved (~ 180 °C) and the exposure to weathering and traffic loading during binder life-time, modified bitumens may undergo a deterioration of the properties because of ageing processes (oxidation of maltene compounds and volatile loss) and polymer degradation [3, 4]. Furthermore, taking into account that polymer-modified bitumens are usually formulated with thermodynamically incompatible materials, phase separation usually happens during their storage at high temperatures leading to transportation problems [5].

Recently, the use of reactive modifiers has proven to improve bitumen-polymer compatibility and may reduce the amount of additives required. The improvement in the thermomechanical behaviour and storage stability takes place because these reactive modifiers are capable of forming chemical links with some bitumen molecules and build a chemical network [6].

In this sense, it is well-known that despite the chemical complexity of bitumen composition, binder's compounds may be broadly separated by chromatographic techniques in terms of solubility and polarity into the so-called SARA fractions (Saturates, Aromatics, Resins and Asphaltenes). The ordering of these chemical groups to develop the bitumen's microstructure raises a great deal of controversy, and so different models have been proposed in the literature, most of them based on asphaltene precipitation and wax crystallization approaches [7, 8]. However, in this contribution, the colloidal model seems to better explain the possible interactions between the additives and bitumen fractions. According to this model, bitumen microstructure is based on a suspension of asphaltene agglomerates that are grouped to form micelle-like structures solvated by resins and dispersed into the maltene medium (constituted by saturates, aromatics and the rest of resins) [7]. It is important to note that the structuring depends on several factors as the relative content of each of these fractions and its chemical structure, micelle dimensions and interactions among them. Therefore, all these factors determine the thermo-mechanical behaviour of the binder in such a way that the more the bitumen is structured, the higher its stiffness and viscosity.

Traditionally, most of the polymeric modifiers are designed to improve the performance of the resulting bitumen by enhancing the stiffness or elasticity at high in-service temperatures and improving the flexibility at low temperatures. However, recently, the increased production of reclaimed asphalt pavement (RAP) materials during recycling operations has forced to the asphalt industry to seek new rejuvenators or softening agents, in order to revert the drawbacks of the ageing of the pavement and to restore the original properties of the binder. Thus, these agents should ideally reconstitute the binder chemical composition and replenish the volatiles and dispersing oils, while promoting adhesion.

Here, a new perspective for the modification of bitumen is explored, based on the use of amphiphilic reactive surfactants so as to promote microstructural modifications by changing the interactions between the asphaltene aggregates.

Even though the use of amphiphilic surfactants is new in the field of bitumen modification, however, they have been frequently used as dispersing agents for asphaltenes in crude oils to prevent their precipitation in pipelines in transportation operations [9-10]. In general, these additives are polymers formulated with a non-polar chain and a strongly polar functional group such as amide, carbonyl, sulfonic acid, etc. The mechanism of modification is based on the interaction of the polar head group of the surfactants with asphaltenes molecules that further alter the colloidal stability of the dispersion, to promote the association of aggregates into larger clusters. However, as it has reported in the bibliography, the type and the magnitude of the interactions between asphaltenes sites and surfactants play a key role on the dispersion or aggregation of asphaltene structures [10]. In this sense, here, two different reactive surfactants having similar tail lengths but different polar reactive heads (sulfonic acid or succinic anhydride groups) have been considered for bitumen modification. Blends of bitumen with 3 wt% additive have been prepared and analysed by means of rheological, thermal and analytical techniques.

2. EXPERIMENTAL

A neat bitumen with a penetration grade of 13/22, supplied by REPSOL (Spain) was used as base material for additive modification. Table 1 gathers its penetration value, ring and ball softening point and temperature when $G^*/\sin\delta = 1$ kPa. The chemical composition in terms of SARA fractions is as follows: 4.0 wt.% saturates, 52.2 wt.% aromatics, 17.4 wt.% resins and 26.6 wt.% asphaltenes.

The following surfactants/reagents were used as modifying agents: succinic anhydride (SA), dodecylsuccinic anhydride (DSA), dodecyl-benzenesulfonic acid (DBSA) and its sodium salt, sodium dodecyl-benzenesulfonate (DBSS), all of them supplied by Sigma-Aldrich. A schematic representation of their chemical structure is shown in Figure 1.

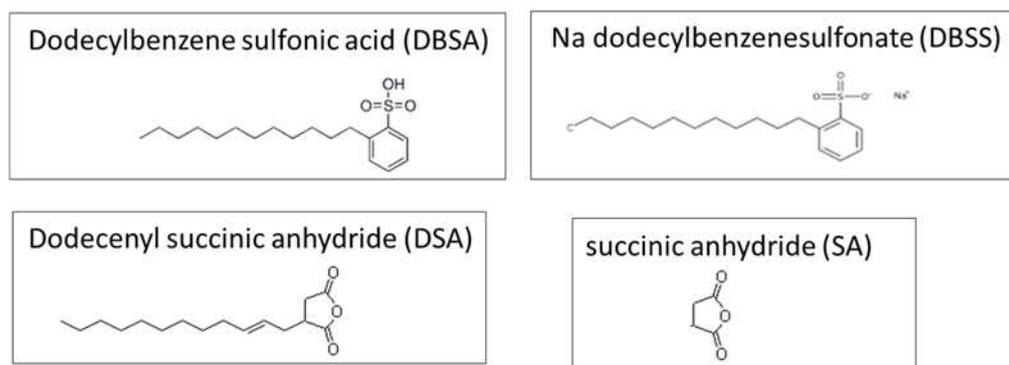


Figure 1. Illustration of the chemical structure of the additives.

Modified bitumens were obtained by melt blending at 150°C for 1 h, by immersion in a recirculating oil digital bath using a low shear mixer composed of a 50 mm four-bladed impeller, coupled to the blending device “IKA RW20”, with stirring speeds of 800–1000 rpm. In general, the concentration of all surfactants (DBSA, DBSS and DSA) was fixed at 3 wt.% whereas SA contents was 1.127 wt.% which is the equivalent molar concentration of the reactive group. In addition, in order to evaluate the ageing effects of processing conditions (150°C, and 1 h) on the resulting properties, a blank sample of neat bitumen with no additive was also processed.

Steady-state viscous flow tests were performed on all samples at 60 °C in a controlled stress rheometer (Physica MCR-301, Anton Paar, Austria). Temperature sweep tests under oscillatory shear, at a frequency of 10 rad/s, were conducted using the same device. A continuous heating ramp was applied at 1 K/min, from 30 °C up to 130°C. Previously, strain sweeps were carried out to ensure a linear viscoelastic response within the entire temperature interval applied. Smooth plate-and-plate geometry, with 25 mm diameter and a gap size of 1 mm, was used for the rheological tests. Before testing, in every case, samples were allowed to rest for at least 20 min.

Conventional tests (penetration grade and ring and ball softening temperature) were performed according to the European Standards UNE-EN 1426 and UNE-EN 1427 respectively.

3. RESULTS AND DISCUSSION

3.1. Thermomechanical behaviour

Firstly, a preliminary study based on conventional tests was carried out in order to analyse the potential modification of the selected reactive surfactants and the influence of processing conditions (blank samples). As presented in Table 1, the combined effect of time and temperature gives rise to a slight hardening of the neat bitumen, as evidenced by the lower penetration and higher softening temperature of the blank samples. Therefore, the influence of the modifying agents is better to be analysed by comparing with the non-modified sample submitted to the same processing protocol. According to this, Table 1 also illustrates that reactive surfactants exert a quite different modification of the technological properties. Then, the addition of alkylbenzene sulfonic acid surfactant (DBSA) leads to a decrease of 3 dmm in penetration and a rise of 4°C in softening temperature whereas its sodium salt (DBSS) hardly modify them. By contrast, the alkenyl succinic anhydride DSA produces an opposite effect revealed by a slight penetration increase and a clear drop of 4°C in ring and ball softening point while the modification with succinic anhydride (SA) yields a different evolution. Therefore, DBSA appears to act as a stiffening agent, improving the intermediate and high in-service properties whereas DSA seems to produce a softening of the binder after modification.

Table 1. Penetration, ring and ball softening point and temperature when $G^*/\sin\delta = 1$ kPa and $=2.2$ kPa of neat and modified bitumens

Sample	Pen, (dmm)	T _{R&B} , (°C)	T _{G*/sinδ = 1 kPa} (°C)	T _{G*/sinδ = 2.2 kPa} (°C)
B 13/22	17	62	84.4	77.0
Blank 150°C	15	64	85.0	77.8
3% DBSA	12	68	92.4	85.6
3% DBSS	15	65	85.8	78.7
3% DSA	16	60	80.3	74.5
3% SA	14	65	86.5	79.3

The effects of both additives at high in-service temperatures may be analysed by means of the flow curves at 60°C (Figure 2). In general, all samples show a wide Newtonian plateau, followed by a decay of the viscosity, which corresponds to a shear-thinning zone. When analysing unmodified binder, it is clear that blank sample only undergoes a slight increase in viscosity, due to bitumen oxidation during processing. However, DBSA modified bitumen

presents a noticeable increase of the Newtonian viscosity while, the critical shear rate of the onset of the shear thinning region is shifted toward lower rate values. This result may attributed to a viscosity building effect due to the development of a more complex microstructure after modification.

On the contrary, DSA-modified bitumen clearly presents a notable drop in viscosity values and a clear increase of the above mentioned critical shear rate, and therefore, this surfactant may function as a binder softener at this temperature.

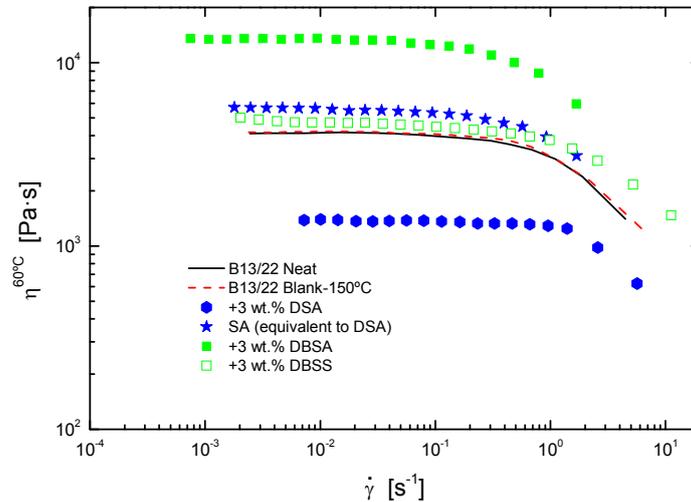


Figure 2: Viscous flow curves, at 60°C, for neat and modified binders.

In order to characterise the thermorheological behaviour in a wide temperature range, temperature sweep tests in oscillatory shear at 10 rad/s were also performed on all samples. In this sense, Figure 3 presents the evolution with temperature of $G^*/\sin\delta$. This is probably the most widely used rheological rutting parameter, proposed by the Strategic Highway Research Program (SHRP) because its magnitude increases with higher complex modulus values (frequently correlated with binder stiffness) and low phase angle (inversely proportional to the stored energy in the deformation cycle and therefore to sample elasticity). In general, Figure 3 points out that no anomalous behaviour was observed and all binder show the well-known direct transition from the glassy to the Newtonian region. Moreover, Figure 3 reveals that, the previously-reported opposite modification effects of DBSA and DSA, are now observed in the whole experimental interval, from 30 to 130°C. Consequently, from ambient to high in-service temperatures DBSA yields a remarkable increase of $G^*/\sin\delta$ whereas DSA shifts this function to lower values.

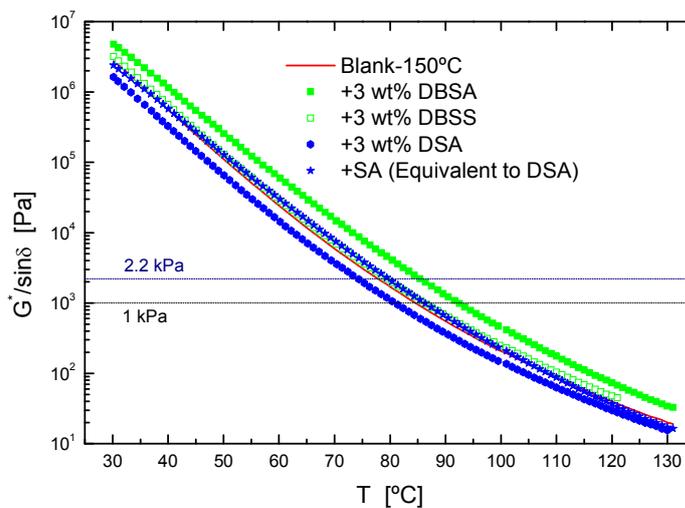


Figure 3: Evolution of the rutting parameter with temperature for selected binders.

From a performance perspective, the application fields of both additives are also different. Thus, despite its low molecular weight, DBSA can be considered an effective modifying agent because its addition to bitumen, at low concentration (3 wt.%), brings about a notable enhancement of the viscous flow behaviour, at 60 °C, and viscoelastic response in a wide temperature range. Therefore, an improved performance of the resulting pavement is expected, especially at high in-service temperatures. In this sense, Table 1 reveals that the high in-service temperature AASHTO rutting parameter ($G^*/\sin\delta$), exhibits a higher value of temperature, at 1 kPa and 2.2 kPa, after DBSA modification, indicating an enhanced rutting resistance.

By contrast, given the capacity of DSA to reduce binder viscosity and stiffness, this additive may be employed as a softening or rejuvenating agent of aged bitumen, in order to restore its original properties deteriorated over time because of traffic loading, weathering conditions and environmental factors.

3.2. Chemical interactions and microstructure

From a chemical perspective, despite DBSA and DSA present a similar hydrocarbon aliphatic tail, the modification caused in binder properties is just the opposite. Evidently, this outcome should be related to the reactive head of the surfactant and to the type of physicochemical interactions with bitumen molecules.

In order to shed some light on modification route, bitumens were also modified with the sodium salt of DBSA (DBSS) and with the same molar amount of the polar head of DSA (succinic anhydride, SA).

Rheological results of DBSS modified bitumen in Figures 2 and 3 and Table 1 allow to compare and analyse the influence of the acidic properties of the amphiphile. According to these figures, it is clear that DBSS barely modifies the rheological response of neat bitumen. Taking into account that DBSA and DBSS only differ in the polar group (sulfonic acid or sodium sulfonate), the reported results reveal that acid–base interactions between DBSA and asphaltenes are responsible of the modification. This chemical process takes place through the protonation of heteroatoms in the asphaltenes, leading to ion pairs with a strong ionic bonding [11]. The attachment of DBSA to asphaltenes favours the association of asphaltene molecules/aggregates into larger clusters in bitumen, leading to the formation of new more complex structures that give rise to the enhancement of the rheological properties.

On the other hand, the sole addition of SA leads to a slight increase of the stationary viscosity at 60°C (Figure 2) and $G^*/\sin\delta$ (Figure 3) while DSA yields a notable reduction of these parameters. In this case, the interactions happens by chemical reactions involving the anhydride with hydroxyl and amine groups of polar bitumen molecules. Therefore, DSA and SA are linked to these polar bitumen compounds (mainly asphaltenes) via covalent bonds that present a considerably lower polarity than ionic pairs of DBSA and, consequently, are unable to promote asphaltene aggregation [12]. As for DSA modified bitumen, the presence of the non-polar long alkyl chain, which is oriented outwards, acts as a lyophilic steric barrier against further interaction, inhibiting asphaltene association and aggregate growing into larger structures. Therefore, these physicochemical processes change the colloidal stability of the bitumen leading to a significant reduction in the degree of microstructural complexity and the reported softening of the system.

4. CONCLUSIONS

The chosen reactive surfactants (dodecyl succinic anhydride, DSA, and dodecylbenzenesulfonic acid, DBSA) contain a similar aliphatic tail of 12 carbons in length but a different polar reactive head, which causes an opposite modification of the thermorheological response. Thus, DBSA addition produces an increase in viscosity at 60°C and a notable stiffening of the binder in a wide range of temperatures that makes it a potential modifying agent to improve the performance of the resulting pavement. By contrast, bitumen modification with DSA yields a remarkable softening of the binder in the whole experimental window, in such a way that it may be considered a new type of chemical rejuvenator of aged bitumen in pavement recycling operations.

From a chemical and microstructural points of view, the nature of the interactions of the reactive surfactant with bitumen polar molecules seems to be behind the reported opposite behaviour. On the one hand, DBSA brings about strong polar ion pairs that favour asphaltene association and the formation of more complex structures. On the other hand, DSA is bonded via covalent links with much lower polarity that together with the aliphatic tail, hinder the aggregation and change the colloidal stability.

ACKNOWLEDGEMENTS

This work was founded by the MINECO (Economy and competitiveness Ministry of Spain) through the project CTQ2017-89792-R (AEI/FEDER, UE).

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