Towards storage-stable high-content recycled tyre rubber modified bitumen

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Towards storage-stable high-content recycled tyre rubber modified bitumen

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Abstract: The addition of crumb rubber particles as bitumen modifier can be currently considered as a well-established alternative to conventional polymers for bitumen modification. However, Recycle Tyre Rubber (RTR) modified binders still present drawbacks such as poor mix workability and hot storage stability. Within this study the authors try unlocking the full potential of devulcanised tyre rubber-heavy oils blend, named Liquid Rubber (LR), by exploring the possibility of tailoring recycled polymer modified bitumen with unconventional high-content of RTR and designed to overcome the above mentioned technological problems of RTR modified bitumen while keeping its advantages. Results show that LR-bitumen blends incorporating up to 30% RTR in weight of total binder clearly improves useful temperature interval of base bitumen by maintaining solubility values allowing them to be considered stable at hot-storage temperature. Furthermore, the LR modifier allows reducing usual manufacture temperatures up to 30°C by providing superior low and intermediate temperature rheology, however high service temperature properties are improved only at low strain.

Keywords: recycled tyre rubber, Liquid rubber, bitumen modification, storage stability, asphalt rubber, no-agitation wet process
1. INTRODUCTION

Bitumen modification has been carried out during decades in order to enhance performance of conventional binder for asphalt mixtures. Traditionally, synthetic polymers of different nature and functionality are used to enhance the resistance to the main distresses affecting asphalt mixtures by increasing their useful temperature interval (UTI) [1]. However, environmental concerns and economical savings opportunities have promoted the use of recycled modifiers for bitumen. In particular, Recycled Tire Rubber (RTR) has been widely studied due to the high saving of landfill space that its use implies and because of the good performance it has shown as bitumen modifier [1]–[4].

When RTR is used as a modifying agent for bitumen, it is called crumb rubber modifier (CRM), while the method of modifying bitumen with CRM before being incorporated into the mixture is referred to as the Wet Process [5]. Bitumen – CRM interaction is material-specific and depends on a number of basic factors, including processing variables (such as temperature, time and applied shear stress), base binder properties (such as source and eventual use of oil extenders) and CRM properties (such as source, processing methods, particle size and content in binder) [6]–[9].

Depending on the adopted processing system and on the selected materials, the Wet Process leads to two different technologies which main distinction is based on rotational viscosity of the resulting rubberised binder at high temperature. On one hand, Wet process–high viscosity is the traditional and more widely used technology obtained with mainly physical modification process based on the swelling of 0–2mm CRM, reaction temperatures between 160°C and 260°C, reaction time varying from 45 minutes up to few hours and usually low shear processing [9]. The final product allows obtaining a rubberised asphalt mix with benefits that are basically linked to the binder’s increase in elasticity and viscosity at high
temperatures [10], [11]. Rubberised asphalt mixtures obtained with this technology showed longer lasting performance compared to the conventional ones [12], [13]. However, these materials require an accurate blend design and non-conventional continuous agitation during hot storage to keep the RTR particles uniformly distributed. Moreover, they could present several operative drawbacks such low workability, poor binder storage stability and the fumes it emits during the paving process due to high operative temperatures (even 180°C).

The second technology is known as Wet process–No agitation and aims at producing CRM bitumen not occurring in phase separation of the modifier from the binder during storage or transportation. For this purpose, CRM has to be fully digested/dissolved into the bitumen without leaving visibly discrete particles. This process prevents the constant agitation needed in Wet Process-High viscosity and improves particles distribution and hot storage stability of blends. The idea behind Wet-process-No agitation binders is therefore obtaining a technology more similar to polymer modified bitumen rather than the above mentioned Wet Process-High Viscosity. Some successful no-agitation wet process technology, such as terminal blends, are already used however they still need to be manufactured at refineries and do not allow achieving the superior performance provided by both the conventional wet process and polymer modification [5].

The objective of this paper is to investigate the feasibility of unlocking the full potential of a liquid polymer that has the potential to allow bitumen technologist to manufacturing in-house storage-stable rubberised bitumen with very high-content of RTR. The above mentioned liquid polymer was provided by innovator LLC and is named Liquid Rubber (LR). LR is actually a family of semi-solid/fluid materials composed by a very high-percentage of RTR plus other oils. In the recent past some LR was used in concrete [14] as well as bitumen modifier by Fini et al. [15] who tested blends of bitumen and 15% LR showing that it can
enhance its low-temperature characteristics but adversely affects the base bitumen elasticity and thus its resistance to rutting. This investigation goes a step further and investigates the potential of maximising the re-use of RTR in bitumen modification by incorporating LR as modifier in proportions from 5% to 60%. The experimental programme consisted in monitoring high temperature rheology (Rotational viscosity) at different temperatures, as well as assessing service temperature rheological and performance-related properties of the blends. At last, solubility tests have been performed to estimate the behaviours of the blends during hot storage. In order to have a direct feel of the level of modification obtained by using several concentration of LR, the measured properties have been compared with those of the base bitumen as well as with a Styrene-Butadiene-Styrene Modified Bitumen (SBS-MB) currently used for asphalt mixtures.

2. MATERIALS AND METHODS

2.1. Materials

In this study the LR, an innovative modifier incorporating 50% RTR and 50% oils, is blended with a 40/60 bitumen in different proportions from 5 to 60% of the final binder. Liquid Rubber is a technology supplied by Innovators LLC in USA and obtained with a proprietary process composed from a digestion tank, a main reactor and a cooling unit. In the first two tanks the #8 (2.36 mm) fibre and glass free RTR is subjected to a process of devulcanisation and mixed with heavy oils derived from petroleoum and/or soy. The process is customisable, allows having control of the off gases, and has a production rate of 12-25 gal/h of LR. The end product is a sticky visibly homogeneous fluid that varying the composition and processing conditions
can have different viscosities (Figure 1). No other details of the production process have been disclosed to the authors.

As mentioned earlier, two different binders were considered as references for the comparison of LR and bitumen blends, namely: conventional 40/60 penetration grade bitumen (40/60 bitumen) and SBS-polymer modified binder (SBS-MB). Conventional properties of these binders are shown in Table 1. The LR is a modifier not a bitumen and therefore it was decided not to perform its conventional characterisation. Instead a complete rheological characterisation of the high-temperature viscosity (Figure 2) and intermediate-temperature rheology (Figure 5) was carried out. Figure 2 reports the high-temperature viscosity of the LR and the reference material. A significant non-Newtonian behaviour of LR was detected during the test within the temperature range 135°C – 200°C. For this reason, all measurements are referred to a speed of 100 rpm in the rotational viscometer. As a result LR presents viscosity values that are higher than the control binders at all considered temperatures.

<table>
<thead>
<tr>
<th></th>
<th>40/60 bitumen</th>
<th>SBS-MB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration at 25°C (dmm) – EN 1426</td>
<td>46</td>
<td>87</td>
</tr>
<tr>
<td>Softening Point (°C) – EN 1427</td>
<td>50.8</td>
<td>103</td>
</tr>
</tbody>
</table>
2.2. Methods

2.2.1. LR-bitumen blends’ manufacture and high-temperature rheology

Rotational viscosity was the physical parameter controlled during the modification process. Therefore, as starting point, rotational viscosity tests build-up by means of low-shear blending protocol [17] were performed on the 40/60 bitumen and LR separately to assess their high-temperature rheology which in turns provide technical information for the LR-bitumen blend preparation.

Being the modifier in a liquid form, the blends were manufactured with very low-shear (200 rpm) by adapting a Brookfield Viscometer to operate as a mixer providing real-time viscosity measurements under a controlled environment. The use of a Dual helical impeller (Figure 3) allowed enhanced dispersion of the modifier during the mixing process [16]. When rubber and bitumen are being blended, the viscosity of the blend increases up to a maximum value (peak viscosity) and then suffers a plateaux or a noticeable decrease with the reaction time. This stage is recognized as the peak of the modification process and was fixed at the point
where the viscosity did not increase more than 5% within 15 minutes [17]. The mixing was then continued for one hour more in order to ensure the stabilization of properties having a blending time of 75 minutes.

![Figure 3. The Dual Helical impeller adapted by [16]](image)

<table>
<thead>
<tr>
<th>BLENDS NOMENCLATURE</th>
<th>LR content (%m/m)</th>
<th>Processing TEMPERATURE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%LR</td>
<td>5</td>
<td>180</td>
</tr>
<tr>
<td>9%LR</td>
<td>9</td>
<td>180</td>
</tr>
<tr>
<td>29%LR</td>
<td>29</td>
<td>180</td>
</tr>
<tr>
<td>37.5%LR</td>
<td>37.5</td>
<td>180/150</td>
</tr>
<tr>
<td>50%LR</td>
<td>50</td>
<td>180/150</td>
</tr>
<tr>
<td>60%LR</td>
<td>60</td>
<td>180/150</td>
</tr>
</tbody>
</table>

LR percentages (in part of total mass) to blend with conventional bitumen were chosen varying from 5% up to 60%. Blends were produced at 180°C, which is a common manufacture temperature for rubberised binders. However, in order to have a clearer understanding of the modification process and to explore potentials of this modifier, the blends with higher LR percentages (over 29% LR) were also manufactured at 150°C. Figure 3. The Dual Helical impeller adapted by [16]
Table 2 shows the manufactured blends of 40/60 bitumen and LR where LR proportions are expressed in part of total mass.

2.2.2. Estimating storage stability through solubility tests

In order to assess potential storage stability issues of bitumen-LR blends, solubility tests were carried out. Tests were performed with standard configuration (EN 12592:2011). Only for the highest LR content (over 37.50% of the total mass) modified solubility tests were required because tire crumbs were not dissolved completely and remained in particulate form during interaction with bitumen. The modified test is widely used for CRM blends and consists on using a wider sieve size (#200 - 75µm) [19]. This sieve prevents the equipment from getting blocked due to bigger insoluble particles arising from the difficulties in the digestion/breaking down of RTR particles during the manufacturing process of the blends.

2.2.3. Service temperature advanced rheological investigation

The core of the assessment was performed through rheological measurements carried out by means of Dynamic Shear Rheometer (DSR) tests at asphalt mixtures service temperatures. The controls and manufactured bitumen-LR blends were subjected to frequency/temperature sweeps from 0.1 to 10 Hz and 0 to 80°C within their linear-viscoelastic range of strain. In these tests, binders’ rheological properties were measured in terms of the norm of the complex (shear) modulus, $|G^*|$ (Pa), and phase angle (viscoelastic balance of rheological behaviour), $\delta$ (°). Once measured, the data were used together with the time-temperature-superposition-principle (TTSP) and shift factors to produce master curves at 30°C. At this point, only the blends judged to be the most promising were selected to continue with low-temperature properties characterisation and performance-related properties.
2.2.4. Performance-related tests and low-temperature characterisation

Multiple Stress Creep Recovery tests (MSCR) according to ASHTO T 350-14 and Time Sweep according to J.P Planche et al. [18] tests were performed in order to evaluate respectively rutting and fatigue resistance of binders. Both tests are performed in the DSR. MSCR test [20] is used to assess binder ability to recover deformation, and consequently, their potential resistance to rutting in the mixture. The test consists on the application of ten creep-recovery cycles to a sample at different stress levels. Each cycle lasts 10 seconds, during which the stress is applied for 1 second (creep) and then the sample is allowed to recover during 9 seconds (recovery). In this study, two levels of stress are considered: 0.1kPa and 3.2kPa. In this sense, binders are evaluated within and without the linear-viscoelastic response range. Tests were performed at 60ºC by using the 25 mm parallel-plate geometry in the DSR.

On the other hand, Time Sweep is used to evaluate fatigue resistance [18]. In this test, binder samples are subjected to a cyclic load in the DSR until failure. Failure criteria was selected as the cycle in which the initial norm of the complex modulus drops 50% [19],[20], [21]. Tests were carried out in stress-controlled mode at a frequency of 10Hz. Binders were tested at 20ºC, which is an intermediate temperature at which fatigue phenomenon might take place, and using the 8 mm parallel-plate geometry. Fraass Breaking point of the best LR-bitumen blends was obtained according to the EN 12593:2015 in order to complete their characterisation in the whole range of temperatures.

3. RESULTS AND DISCUSSION

3.1. LR-bitumen blends’ manufacturing and high temperature rheology

Figure 4 shows the high-temperature viscosity measurements of the LR-bitumen blends.
Viscosity values were taken during the 75 minute – manufacture of the blends at 180°C and
150°C. It can be observed that LR provides an appreciable modification of bitumen properties (higher viscosity) only when at least 37.5% of mass of bitumen is replaced. For all cases, LR allowed achieving peak viscosity and properties stabilisation in less than 20 minutes. In addition, it can be said that LR is a very different modifier from the CRM. Results show that, regardless of the processing temperature, the reaction between LR and bitumen does not involve any swelling process and/or devulcanisation, depolymerisation and further digestion that are typical of bitumen modification with CRM [5]. Furthermore, LR-bitumen blends manufactured at 150°C do not show undergoing a different modification process than those manufactured at 180°C. This temperature is well below the typical processing temperature of CRM-bitumen blends.

![Figure 4. Rotational viscosity at 100 rpm of the reference materials vs. temperature; (b) Rotational viscosity of the blends vs. manufacture time](image)

In Figure 4 it can also be observed that final viscosity of the blends is always below 1500 mPa.s (even with 60% LR and 150°C manufacture temperature), which is a typical value for conventional CRM modification [5]. These results show that LR-bitumen blends are far from
being classified as High Viscosity - Wet process and that despite of the high amount of recycled tire rubber that they contain, they could provide good workability towards a significant reduction in asphalt concrete manufacturing temperatures and relative energy consumption.

3.2. Hot storage stability through Solubility tests results

Solubility tests were carried out for the blends manufactured at 180°C. Modified EN 12592 permitted to easily perform solubility tests of the blends with higher LR content. Results are shown in Table 3 where it can be observed that LR-bitumen blends have solubility almost comparable to the neat bitumen. This fact would be favourable for hot storage stability and allow classifying these binders as No Agitation – Wet process. In order to check the effect of processing temperature, the 29% LHR blend manufactured at 150°C was also subjected to solubility test showing that solubility is not affected by processing temperature. These results were considered satisfactory to reach a conclusion on storage stability, hence solubility tests on the LR itself were not been carried out.

<table>
<thead>
<tr>
<th>BLEND</th>
<th>% Soluble Material</th>
<th>% Insoluble Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS-MB</td>
<td>99.15</td>
<td>0.85</td>
</tr>
<tr>
<td>Neat</td>
<td>99.93</td>
<td>0.07</td>
</tr>
<tr>
<td>5% LR</td>
<td>99.44</td>
<td>0.56</td>
</tr>
<tr>
<td>9% LR</td>
<td>99.05</td>
<td>0.95</td>
</tr>
<tr>
<td>29% LR</td>
<td>97.62</td>
<td>2.38</td>
</tr>
<tr>
<td>29% LR (150°C)</td>
<td>97.75</td>
<td>2.25</td>
</tr>
<tr>
<td>37.5% LR*</td>
<td>98.72</td>
<td>1.28</td>
</tr>
<tr>
<td>50% LR*</td>
<td>98.26</td>
<td>1.74</td>
</tr>
<tr>
<td>60% LR*</td>
<td>97.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

* Solubility tests performed with the modified configuration
Advanced rheological characterisation was performed for the reference materials and LR-bitumen blends. However, only those blends showing a significant modification of bitumen properties are shown in Figure 5 in terms of Black Diagrams and master curves at 30°C.

LR shows to be a complex material that is non-Newtonian and non-thermo-rheologically simple. Black Diagrams are the rheology fingerprint of a material and LR-bitumen blends have comparable behaviour to the SBS-MB. In particular, the blend with 60% of LR shows having a very similar rheology to SBS-MB with similar stiffness and elasticity over the whole range of temperatures and frequencies. LR provides the blends with the benefit of a more viscous behaviour at low temperatures (higher value of phase angle), but with a much lower stiffness, especially at high temperatures (low frequencies). Higher content of LR leads to blends with higher elasticity but lower stiffness over the whole range of temperature and frequencies.

This is in line with the composition of the modifier that provides an overall decrease in rigidity at intermediate and low temperatures, due to the enhanced elastic behaviour conferred by the rubber and decrease in stiffness due to the oils fraction.

Figure 5 (b) shows that Black diagrams of the blends do not change whether they have been manufactured at 150°C instead of at 180°C. In this sense, LR allows modifying bitumen with high RTR content at a 30°C lower temperature than that used in classical processes with CRM.
Figure 5. (a,b) Black diagrams; (c) Complex modulus master curves at 30°C; (d) Phase angle master curves at 30°C

### 3.4. Performance-related and low-temperature properties

MSCR tests and Time Sweeps were carried out to better investigate the performance of the blends to resist different asphalt pavement distresses such as rutting and fatigue. Results are shown in Figure 6.
In Figure 6 (a), within the linear viscoelastic region (0.1 kPa), LR-bitumen blends perform well as indicated by the high recovery that is higher than the 40/60 bitumen and comparable to that of SBS-MB. This result appears to be in contrast to what was found by previous researches [14] and may be due to the nature of the LR or the different modification percentages. As the level of stress increases, the modification is totally vanished and the material properties change. This fact can be attributed to the absence of networking between the LR and the base bitumen which in turns does not sustain higher strains and eventually breaks. The oil agent contained in the LR might be the main factor that makes the modified material softer and even weaker than neat bitumen. Higher content of LR leads to blends with lower recovery. This shows an absence of a network between the modifier and the bitumen, which is distinctive of commercially used SBS-MB. For this reason, 60% LR blend was discarded for further tests.
Fatigue results are displayed in Figure 5 (b) and show that LR blends have similar or lower slopes than the 40/60 bitumen, meaning that susceptibility to strain level is not significantly different. However, LR shows having much higher more loading cycles until failure for the same initial strain (more than an order of magnitude), which leads to assess that LR modification greatly improves fatigue life of 40/60 bitumen. On the other hand, when compared to SBS-MB, the fatigue resistance of LR blends is comparable to the SBS-MB only at high strain levels (>10% which happens is pavements with heavy traffic), however, as the initial strain decreases, SBS-MB exhibits much longer fatigue life due to the lower slope of its fatigue law. Therefore, LR-bitumen blends overall significantly increase fatigue-related of conventional bitumen, while it shows the lack of a polymer network when compared to SBS-MB who shows superior fatigue-related properties in both strain susceptibility and fatigue life.
At last, the binders were compared in terms of low-temperature properties. LR-blends low-temperature rheology was deeply investigated in a previous investigation that clearly proved how the oils present in the LR provides significant benefits to the LR-blends [14]. Hence, with the aim of confirming this trend also by looking at conventional properties, in this investigation the Fraass Breaking Point of the different binders was tested. Table 4 displays that LR modification is able to decrease Fraass Breaking point of the bitumen more than 3 times in the case of the 50% LR blend. Furthermore, Fraass breaking points of LR-bitumen blends are comparable or even better than that of SBS-MB. Although this test is not a strictly performance-related test, Fraass breaking point is highly linked to low-temperature cracking resistance of the material [22] and therefore it can be said that overall LR-bitumen blends most-likely will improve low-temperature cracking behaviour of a conventional asphalt pavement to a level comparable or even superior than SBS modified asphalt mixtures.

4. SUMMARY AND CONCLUSIONS

Recycling tyre rubber in asphalt pavement is a successful practice that is unfortunately not use worldwide also due to important technological issues such as workability issues and the lack of storage stability at high-temperatures. Liquid Rubber is a blend of heavy oils and devulcanised recycled tyre rubber that allows an innovative delivery process for incorporating tyre rubber in asphalt mixtures. This technology was explored in few previous investigations, although none of the tried unlocking its full potential and shown that LR can allow manufacturing superior bituminous binder incorporating unconventional high-content of
RTR. For this purpose, conventional bitumen has been modified with different percentages of the modifier, corresponding to up to 30 wt.% of recycled Tyre Rubber. Blends’ manufacturing process was monitored in real-time through high temperatures rotational viscosity. In addition, the effect of using different manufacturing temperatures was evaluated. LR-bitumen blends were studied in terms of rheology, hot storage stability potential, performance-related and low-temperature properties and were compared to the base bitumen and a commercial SBS-MB. The following conclusions can be drawn:

- Overall, the selected LR is a non-Newtonian and non-thermorheologically simple material that significantly decreases bitumen rigidity at low and intermediate temperatures and, at the optimum content, can also provide a moderate increase in resistance to plastic deformation of the base bitumen.

- LR-bitumen blends need much shorter processing time than standard asphalt rubber. In fact, the LR do not show any sign of digestion/swelling during the manufacturing and therefore seems not to require the high processing temperatures needed than for the classical processes with CRM.

- Even with a recycled tyre rubber content of 30% in weight of total binder, these blends have viscosities values well lower those of conventional asphalt rubber binders. This of course can allow to significantly reducing asphalt manufacturing processing temperatures as well as facilitating laying and compaction issues typical of rubberised asphalts.

- LR-bitumen blends have very high solubility that indicates their potential to obtain good storage stability. These facts allow classifying these blends as No Agitation – wet process technology.
LR-bitumen blends exhibit comparable rheology to commercial SBS-MBs. When optimum dosage is achieved they show superior low-temperature properties, due to the presence of heavy oils, longer fatigue-life than conventional bitumen although they generally have not satisfactory stiffness and elastic recovery at high service temperatures. These facts could be both attributed to the lack of structured network which is instead a distinctive characteristic of polymer modified bitumen.

Overall, results showed that liquid rubbers technologies could be already used in many application within the bitumen industry, although further research should focus on investigating the ageing potential of these blends. Currently, authors are also investigating suitable solutions for improving LR-bitumen blends resistance to plastic deformations.

ACKNOWLEDGEMENTS

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