Bitumen performance and chemistry in solvent refined bitumen blends

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Abstract. In years gone past most oil companies in Australia and New Zealand (NZ) developed experts that bridged the divide between refining and paving. This was supported by laboratories in Australia and sometimes Asia. This is no longer the case and many refineries have ceased bitumen production or closed. With the market moving towards imports and control to supply companies disconnects on bitumen passing a national specification and performance on the road. This reduces both durability and increases costs. This has been addressed by development in NZ of a performance specification for hot mix asphalt binders (including modified) and work being done on sealing grades. This paper discusses the development of the HMA specification with respect to crude sources and the development of methodologies to assess imported binders for suitability in all applications including emulsion. The conclusion is that bitumen quality may be maintained by use of these methodologies that include, chromatographic analysis, measurement of thermodynamic internal stability (Heithaus), aging, and Dynamic Shear Rheometry testing and mix performance testing in the laboratory. This forms a regime capable of use in any context and this leads to better durability of surfaces and extended service life.

1. Introduction

Bitumen in New Zealand (NZ) has two sources, the first is the New Zealand Refining Company (NZRC) and the second is imports, these may come from any part of the world. The penetration specification of New Zealand NZTA M-1 [1] is an empirical consistency specification originally based on Safaniya (Saudi heavy crude) based partially blown bitumen and then adjusted in 2006. This was in an attempt to widen the allowed bitumen imports. The result was achieved by relaxing the viscosity specification slightly but without reference to performance. The result was thermally susceptible bitumen being introduced that created issues of flushing, rutting, tenderness and shoving in early life. In NZ the primary premature failure mode of new surfaces, both chip seal and hot mixed asphalt (HMA) are related to higher temperatures and heavy traffic. To address long term deformation, a new specification requirement based on wheel tracking was introduced in 2006. The industry tolerated this issue until it became obvious that some complaint penetration bitumen asphalt grades rutted prematurely in service and could not pass the basic requirements of the specifications and produce a compliant design for heavily trafficked roads. It was also clear that early tenderness made compliance with field volumetric specifications difficult. This paper discusses the steps taken to ensure that correct mixes could be designed and applied for durable surfacing of NZ roads.
2. Background and literature review

The relationship between bitumen chemistry and performance has been studied extensively for many decades. The major collection of this work was during the SHRP program in USA in the 1990’s. The effect of crude source was described by Harnsberger [2] who reported crudes as an important contributor to field performance even within a given Performance Grading (PG grading).

In earlier work [3] the relationship between bitumen composition and HMA properties was considered using Dynamic Shear Rheometry, and testing laboratory mixes using wheel tracking and conventional asphalt testing. This showed that bitumens made with lighter crudes produced higher phase angles in DSR testing. In turn, mixes were produced that were more shear and temperature susceptible in laboratory testing leading to flushing and tenderness in application. Premature failure under traffic via shoving and rutting followed.

The conclusion, that simply blending to penetration was insufficient to ensure HMA performance in heavy traffic and high temperature conditions has led to a new specification NZTA M-1A [4,5] that uses creep compliance and other rheological parameters to relate to performance of HMA, being based on NZTA M-10 2014 [6] performance related variables such as deformation (wheel tracking) fatigue (4 point bending) plus the Asphalt Performance Mix tester (AMPT) [7] overlay, dynamic modulus and push pull fatigue testing.

Modern refineries are collections of processing units balanced by refinery economics to produce the most advantageous product mix. Bitumen is rarely a main aim except in specialty refiners such as Nynas in Europe. In NZ the refinery has clients who provide crudes for processing into products for downstream marketing. The main processing routes for the NZRC refinery are shown in Figure 1. In this process bitumen is only shipped in small parcel sizes although demand is continuous. Added complications are crude shipment, refinery scheduling, tank segregation, blending and ship loading.

![Figure 1. Refinery process NZRC New Zealand.](image)

In NZRC only the soft grade (180/200 penetration) is made from certified heavy bitumen crudes - Ratawi and Arab Heavy. In some instances it is of higher penetration than specification and Butane pitch (BDA), a residue of general purpose crude processing that is solvent refined, is used in small percentages. This of course means the 180/200 is no longer straight run and can have variable rheology. The general purpose crudes used are light to extra light in nature. Classification uses the American petroleum institute consistency rating (API) of crudes. This measures degrees API which is an inverse function of its specific gravity relative to that of water. That is the greater the API, the lighter the crude.
Heavy is 29 and less, Medium is 29-32, Light is 32-34, Extra Light is 36-41 and Superlight is 49-52. The harder grade is made from 180/200 blown to 40/50 and then mixed with a blend of BDA (50%) and 180/200 – so called New Route bitumen 40/50 (NR). This BDA and its variability in composition is responsible for higher levels of thermal susceptibility in blends. Thus a high performing bitumen composition has a low tolerance for BDA addition. Solvent modified materials such as BDA have been shown in earlier work to create issues for emulsion stability [3] due to the chemical composition being rich in aromatic oils. For the same reasons BDA blends can produce hot mixed asphalts that do not perform satisfactorily in the field. The way in which it is blended affects the total composition of the final blended binder. Despite its low penetration the BDA has lower elasticity (as measured by phase angle using AASHTO T315 and Dynamic shear rheometry [8]) at any given temperature which leads to greater thermal and shear susceptibility in the final bitumen.

3. Research motivation and objectives
The issue that arises is one of specification and screening, it also touches on areas of making a given bitumen work in the required application. This research is an ongoing direction for the authors that includes aspects of renewable resources, durability in field situations and modification. The paper reports this development in the context of development of an assessment framework based on chemical knowledge and understanding of mix performance.

4. Test methods and material preparation
Bitumen is a complex material chemically. Being drawn from naturally occurring crudes it will vary both in component percentages based on SARA (Saturates, Aromatics, Resins and Asphaltenes) fractions but also in the chemistry of those fractions. This is due to differing levels of polar associations and the level and type of hetero atoms. Sulphur in the form of sulphoxides and other compounds is particularly influential on mechanical properties [9].

This paper uses Dynamic Shear Rheometry (DSR) AASHTO T315 testing [8], Multiple Stress Creep Recovery Test (MSCR) testing AASHTO TP70 [10] to look at differences in base binder rheology with differing BDA levels and composition. AASHTO T315 employs a fixed strain level and frequency based on field shear levels, and varying temperature to measure phase angle and complex modulus. MSCR uses an oscillatory test method to determine creep compliance. Mix performance is characterised by wheel tracking as per Austroads AGPT-T231 [11]. Fractionation by Iatroscan is carried out using an established methodology [3]. Work reported by the authors in this paper discussed the background of this in detail including the use of TLC- FID Iatroscan methodology. Heithaus testing was carried out using ASTM 6703 [12] and the Western Research Institute approach of Pauli [13]. The Heithaus parameters are from ASTM D6703. The most useful parameter is “P” the bitumen state of peptisation-internal stability. This is a combination of the ability of associated species (asphaltenes) to be stable in the dispersed medium (p_0) and the ability of the dispersing medium to disperse the associated species (p_p).

Moisture sensitivity, resilient modulus, beam fatigue testing and overlay testing were also measured on the HMA samples but this is not reported in this paper. However the results indicated that the effect of softening by BDA does not reduce fatigue life, overlay crack resistance, or increase moisture sensitivity, but resilient modulus is reduced. The bitumen samples used are shown in Table 1. The API ratings shown are: XL - extra light, L- light, M - medium, H - heavy.
Table 1. Information on crude type used in BDA.

| Sample | Crude type | % BDA in 40/50 |
|--------|------------|----------------|
| 1      | XL         | 2.5            |
| 2      | L          | 11.5           |
| 3      | L          | 17             |
| 4      | L          | 20             |
| 5      | L          | 25             |
| 6      | L          | 26.5           |
| 7      | L          | 34.5           |
| 8      | XL         | 38.5           |
| 9      | M          | 27.5           |
| 10     | M          | 33.5           |
| 11     | M          | 20.5           |
| 12     | H          | 0              |

5. Test results, analysis, and discussion

5.1 Effect on structure of BDA
The effects of BDA on binder rheology are shown in Figures 2-5. Figure 2 shows the phase angle relationship for % BDA. This clearly shows that the higher percentage BDA has higher phase angles and hence is less structured (Note that some lines have been removed for clarity). Even small amounts of BDA have a significant effect on the structure. Figure 3 compares like BDA percentages but with different crude bases in the BDA. The comparison shows that phase angle is higher for 40/50 made with the lighter crude based BDA.

Figure 2. Phase angle relationship for BDA addition.
5.2 Effect on Stiffness of BDA

The results shown in figure 4 and 5 for Complex modulus (G*) follows the same trend and that higher BDA levels result in a decrease in elevated service temperature stiffness and higher low service temperature stiffness compared to well performed bitumen. Higher viscous modulus (G’’) and lower elastic modulus (G’) indicate that the bitumen will be less deformation resistant and more prone to crack.

**Figure 3.** Effect of crude base on phase angle.

**Figure 4.** Complex modulus for different crudes.
5.3 Composition changes

The Iatroscan measures SARA fractions and in this analysis the total structuring phase is defined as resins A plus resins B and the total dispersing phase as saturates plus aromatics. Figure 6 indicates, that as BDA increases the associated or structuring phase is reduced as the dispersing phase increases this can lead to instability in the bitumen matrix.

This is also reflected in the Heithaus tests as per ASTM D6703 (using Western Research procedure) parameters. The total stability factor P is shown in Figure 7.
Figure 7. Thermodynamic stability by Heithaus test ASTM D6703.

A “P” value of around 3 is the normal point of internal instability of a binder that has been found, in field materials, to be an issue, with respect to deformation and cracking resistance, when blended to a penetration grade of 60/70. When made into blends to a penetration grade of 60/70, the grade of binder tested on MSCR showed that with same base straight run 180/200 the PG grade went from PG64H to PG64S at around 30% BDA in the 40/50 blend. Wheel tracking results are reported in Figure 8 and show that, increasing BDA content resulted in increased deformation. It has been established that this correlates with field observations of increased propensity to flush, rut and exhibit tenderness in laying [3] (Note that this refers to 60/70 binders blended to NZTA M-1 grade using the same 180/200 straight run heavy crude base bitumen and the 40/50 with varying BDA).

Figure 8. Wheel tracking results.
6. Conclusions and recommendations

1. The composition of bitumen determines its rheology.
2. Solvent refined materials such as BDA while being able to be used in blends to penetration grades can result in compositions that are unbalanced and hence created rheological properties unfavorable to performance.
3. The effects are crude dependent, lighter crudes give poorer results.
4. Performance specifications have been shown to address these issues.

References

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