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Impact of bitumen and aggregate composition on stripping in bituminous mixtures

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Abstract The impact of bitumen and aggregate composition on stripping was investigated using four bitumens and four aggregates. Moisture sensitivity was assessed based on retained resilient modulus and tensile strength ratio (MRR and TSR, respectively). The results indicate that mixtures from the bitumen with a high acid number exhibited high resilient modulus and tensile strength in the dry condition for all the aggregates. In wet condition, this conclusion did also hold except for one aggregate. Regarding penetration grade, mixtures made with lower penetration grade bitumen exhibited higher resilient modulus and tensile strength, in dry and wet conditions, than those of higher penetration grade. Bitumen characteristics like acid number, penetration grade and molecular size distribution did not influence moisture sensitivity. Mixtures with aggregates containing alkali metals (sodium and potassium) exhibited relatively high moisture sensitivity, regardless of the bitumen used. In contrast, indications of moisture sensitivity were not apparent in mixtures made with aggregates containing calcium, magnesium and iron. Data analysis revealed that variability in moisture sensitivity is attributed to aggregate rather than bitumen. No significant interaction effect between bitumen and aggregate was found on moisture sensitivity. The results indicated good correlation between MRR and TSR in ranking mixtures for stripping.

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Résumé *L'effet sur l'arrachement, du type de bitume et de la composition des granulats, a été étudié à pour quatre bitumes et quatre types de granulats. La sensibilité à l'humidité a été analysée à l'aide du rapport des modules résilients humide et sec (RMR) et du rapport de résistances en traction humide et sec (RRT).Les résultats montrent que les enrobés formulés à partir de bitume à fort "indice d'acide" présentent des valeurs importantes en module et en résistance, lorsque les granulats sont secs. En atmosphère humide, cette conclusion est respectée, excepté pour un type de granulat. Les enrobés formulés avec des bitumes à faible pénétration présentent des modules et résistances plus importants que ceux fabriqués à base de bitume plus dur, en conditions sèche et humide. Les caractéristiques du bitume comme l'indice d'acide, la pénétrabilité et la distribution de la taille des molécules n'ont aucune influence sur la sensibilité à l'humidité. Les enrobés à base de granulats contenant des alcalins (sodium et potassium) présentent une sensibilité à l'humidité relativement importante, indépendamment du bitume utilisé. En revanche, aucune sensibilité n'est visible sur les enrobés formulés à partir de granulats contenant du calcium, du magnésium et du fer. Les analyses des données montrent que ce changement de sensibilité à l'humidité est dû aux granulats plutôt qu'au bitume. Aucun effet significatif sur la sensibilité à l'humidité, dû à une interaction entre le bitume et les granulats,* *n'a été observé. Les résultats traduisent une bonne corrélation entre le RMR et le RRT pour classer les enrobés relativement à la propriété d'arrachement des granulats.*

1. Introduction

Bituminous pavements are subjected to very high stresses due to the influence of heavy vehicle loading. More recently, there has been a rise in this loading because of increase in tyre pressures, switch from cross-ply to radial-ply tyres, replacement of dual tyres by wide base single tyres (especially in Europe), and others [1]. This load increase requires use of bituminous mixtures with high and durable resilient modulus and tensile strength, both of which most probably depend on the nature of aggregate particles, the interstitial bitumen/mastic and the strength of the bond at their interface. Some literature consider aggregate to be a more dominant factor than bitumen, for example [2]. Accordingly, adhesion between bitumen and aggregate, needs to be strong and durable under all prevailing conditions of traffic and environment. Moisture damage, in form of stripping, is among the factors that may influence adhesion at the bitumen/aggregate interface. Whether stripping occurs prematurely or in a reasonable range of service life, the required repair costs could probably be reduced through judicious material selection.

A review of literature reveals extensive research previously undertaken to determine mechanisms of interaction at the bitumen/aggregate interface in dry and wet conditions [3–7]. There are differences in findings from such studies. For example, the most readily adsorbed bitumen component onto aggregate sites was reported as *carboxylic acids* by Plancher et al. [5], *pyridinics* by Petersen et al. [8] and *sulfoxides* by Curtis et al. [6]. Different results are similarly reported on the most readily desorbed bitumen components due to action of water. All these inconsistent findings lead to continuing debate, indicating that the problem of stripping is still complex and far from being fully understood. The strength of the interfacial bond, in both dry and wet conditions, appears to relate to the composition of the bitumen and the aggregate that share the interface [9]. This is because adhesion arises because of the interaction of polar components in the bitumen with the polar aggregate surface. Accordingly, understanding how interfacial adhesive strength and its moisture-related loss, relate to interaction of fundamental composition of bitumen and aggregates, can be valuable in materials selection and mix design deliberations. See Bagampadde et al. [10] for further details regarding important aspects of bitumen and aggregates, and how they relate to moisture damage.

The primary aim of the study reported in this paper, was to investigate the influence of bitumen and aggregate composition on interfacial adhesion and water sensitivity of bituminous mixtures. The authors speculate that loss of interfacial adhesion reduces mixture resilient modulus and tensile strength. This has also been indicated previously [11]. Therefore, the method used in investigating moisture sensitivity involved relating the water-induced reduction of the two fundamental mixture properties to combinations of diverse bitumen and aggregate compositions. In this study, four different bitumens from diverse sources and four different types of aggregates were employed.

2. Experimental

2.1. Materials

The four different bitumens used in this study were identified by codes BIT1, BIT2, BIT3 and BIT4. Two of the bitumens (BIT1 and BIT2) were from the Middle East, and BIT3 was from Laguna, Venezuela. The fourth bitumen (BIT4) was supplied by Nynäs Petroleum Research Company, Nynäshamn, Sweden, and its source was unknown. The four aggregates employed in this investigation were supplied by different contractors, and are typically used in a temperate climate. The delivered aggregate batches were sieved and reconstituted to fit specified standard base coarse aggregate having a continuous grading and maximum size of 16 mm as shown in Fig. 1.The aggregates were assigned identification codes AG1, AG2, AG3 and AG4.

2.2. Test procedures

2.2.1. Bitumen

Bitumen physical properties were determined using standard procedures and the results are shown in Table 1.As can be seen, three of the bitumens are of 70/100 grade and the fourth is of 50/70 grade. Viscoelastic properties of bitumens were determined using

Table 1 Physical characteristics of the studied bitumens

Property	Bitumen code Bitumen source Bitumen grade[a]	BIT1 Middle East 70/100	BIT2 Middle East 70/100	BIT3 Venezuela 70/100	BIT4 Unknown 50/70
Penetration, 25°C, 100 g/5s, (dmm)[b]		86	84	84	69
Softening Point, (°C)[c]		47.4	48.5	44.5	48.9
Ductility, 25°C, (cm)[d]		115	121	136	106
Brookfield viscosity, 135°C, (mPa.s)[e]		346	352	302	460
Complex modulus at 10°C (MPa)		6.4	5.1	4.8	11.5
Phase angle at 10°C (degrees)		47	46	55	41

[a]EN 12591:1999; [b]ASTM D5; [c]ASTM D36; [d]ASTM D113; [e]ASTM D4402

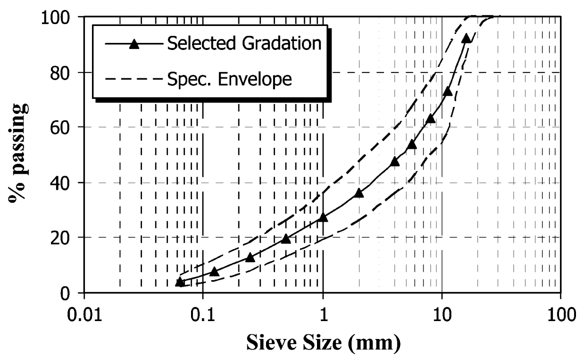

Fig. 1 Reconstituted size distribution used (Road 94).

dynamic mechanical analysis (DMA). The viscoelastic measurements were made using a dynamic shear rheometer (Rheometrics-RDA II) instrument with a sinusoidal strain set at a frequency of 1 rad/s (0.159 Hz) and temperature sweeps from −30 to 80°C. Parallel plates of diameter 8 mm, separated by a gap of 1.5 mm, were used. In each test, about 0.2 g of bitumen sample was applied to the bottom plate, covering the entire surface, and then mounted into the rheometer. After ensuring that the bitumen had reached the softening point, the top plate was carefully placed onto the sample, followed by neat trimming of the protruding parts of the sandwiched bitumen. After adjusting the final gap to 1.5 mm, a sinusoidal strain was applied by an actuator. Viscoelastic parameters, complex modulus (G*) and phase angle (δ), were obtained by a computer directly connected to the rheometer. The results of complex modulus and phase angle at 10°C are shown in Table 1. The temperature of 10°C is the one at which mixtures were tested for resilient modulus and tensile strength, as described later. These data show that the bitumens have varied viscoelastic behaviour at this temperature.

Gel-permeation chromatography (GPC) was used to characterize the bitumens, by separating its constituents on the basis of molecular size. Solutions of bitumen (5% by weight) in tetrahydrofuran (THF) were passed through a system of ultra-styragel columns. The pores of the gel exclude molecules larger than a certain critical size, which consequently take a shorter distance through the column. As a result, the bitumen components are eluted in order of decreasing size. Calibration was done using a broad molecular weight polystyrene standard and detection was automated.

Functional group analysis was used to obtain the functional groups of interest in the study. These data were collected using Fourier transform infrared (FTIR) spectroscopy by employing an infinity 60AR spectrometer (Mattson, resolution 0.125 cm^{-1}). Bitumen solutions (5% by weight) were prepared using carbon disulfide (CS_2). Blank (solvent) and sample scans were performed using Attenuated Total Reflectance (ATR) prisms and circular sealed cells of Zinc Selenide (ZnSe) windows. Spectra were obtained in wavenumbers ranging from 3400 to 500 cm^{-1}. Specifically, the absorbance peaks of interest were targeted in the carbonyl region (around 1705 cm^{-1}).

2.2.2. Aggregates

In determining chemical composition, the aggregates were tested for silica, alumina, potassium, sodium, iron, magnesium, calcium and manganese. The compositions (% by weight) of these elements were obtained in terms of oxides, although oxides may not necessarily naturally occur in aggregates [12]. Contents of potassium, sodium, iron, magnesium, calcium and manganese were got by digesting 200 mg of aggregate samples, ground to pass through 100-mesh sieve, with 10 mL of hydrofluoric acid (conc. 40%) reagent mixed with 3 mL of perchloric acid (conc. 70%). The mixture of the acids and sample was heated in a 50 mL beaker for 1 hr on a hot plate having a surface temperature of 200°C and then allowed to cool for 5 min. This procedure was repeated until initial dryness was attained, followed by dilution with distilled water, filtered and finally analyzed using an atomic absorption spectrophotometer. Alumina (Al_2O_3) was determined by a gravimetric method through precipitation of the aggregate with 8-hydroxyquinoline. Silica (SiO_2) was determined by a spectrophotometric method, where the samples were digested by fusion with sodium hydroxide, and the resulting solution complexed with molybdate for analysis.

Aggregate mineralogy was determined by sawing large samples (50 mm × 50 mm), followed by thin sectioning onto glass slides to a nominal 30 μm thickness in readiness for examination. Optical microscopy (400×) was then used to determine colour, grain size and mineral crystals in the aggregates.

Minor phases below a detection limit of 1–2% were not revealed. It was possible to identify the rock names of the aggregates based on the procedure by Strekeisen [13]. The minerals identified included quartz, feldspars, mica and ferromagnesian. Limestone and dolomite aggregates were unfortunately excluded, since they were not available within the region covered.

Macroscopic rock texture analysis of the aggregates was done using a Zeiss Polarizing Microscope. The results of this analysis were as follows:

- AG1 – Medium to coarse grained (2–6 mm), subhedral phaneritic texture.
- AG2 – Fine to medium grained (0.2–2 mm), subhedral to anhedral foliated texture.
- AG3 – Medium to coarse grained porphyritic texture (1–6 mm).
- AG4 – Medium grained (mylonitic texture) – coarser clasts of 60% by volume, medium grained matrix 40% (volume) and crystal sizes in the matrix of 2 mm and size of clasts is 4 mm.

2.2.3. Bituminous mixtures

Mixtures were designed to comply with the Swedish standard AG16 hot mix base material having aggregate nominal maximum size of 16 mm (Road 94). The blended gradation for all the aggregates, as well as the limits, was in accordance with Road 94 (cf. Fig. 1). Typically, 10 kg of each aggregate required to prepare at least five specimens of diameter 100 mm and approximate height 100 mm was heated in an oven at 140°C for four hours. Bitumen was heated at 140°C for one hour before mixing with the aggregate. According to Swedish road standards (Road 94), an AG16 mix may consist of different penetration grade bitumens. Since binder content depends on the bitumen grade, the binder contents for an AG16 mix corresponding to B85 and B60 bitumens are 4.9 and 5.1% by weight, respectively. Consequently, 515 g and 536 g of hot B85 and B60 bitumens, respectively, were added to 10 kg of hot aggregate and mixing was done at 140°C using an electric mixer. The loose mix was put and covered on a hot pan. 2 kg of the loose mix (enough for a specimen 100 mm diameter and about 100 mm height) was placed in a hot compaction mould. Compaction of each specimen was done at 100°C using a gyratory compactor (Model ICT-150R/RB from Finland). The specimen height attained was not exactly 100 mm because during compaction, height was the only variable controlled to attain the targeted air voids content of 7 ± 1 (% by volume) for proper vacuum saturation during conditioning. The compacted specimens were extruded from moulds and allowed to cool at room temperature for 24 hrs. The air voids were checked by measuring the Rice specific gravity (AASHTO T209) and bulk specific gravity (AASHTO T166) of the specimens (cf. volumetric properties of mixtures studied in Table 2). Each specimen was wet sawn into two cylindrical specimens of 100 mm diameter and 40 mm thick, making a total of ten specimens for each bitumen/aggregate combination.

2.3. Moisture sensitivity testing programme

Evaluation of moisture sensitivity of the bituminous mixtures was done in accordance with a procedure closely related to the modified Lottman test (AASHTO-T283). For each bitumen/aggregate combination, ten replicate test specimens were prepared. All the replicates were, as much as practically possible, kept identical with respect to aggregate type, air voids content range, aggregate gradation, level of gyratory compaction, bitumen content, 24 hour storage, and others. The samples were randomly assigned to two groups of five specimens each. One group was kept dry as a control at room temperature, and the second one was

Table 2 Volumetric properties of the mixtures studied

Binder	Aggregate	$G_{mm}{}^{\xi}$	$G_{mb}{}^{\xi}$	Voids (%)	Saturation (%)
BIT1	AG1	2.444	2.271	7.08	73.1
	AG2	2.571	2.396	6.81	65.0
	AG3	2.384	2.214	7.14	60.9
	AG4	2.459	2.304	6.29	62.4
BIT2	AG1	2.373	2.226	6.18	68.3
	AG2	2.630	2.441	7.19	76.7
	AG3	2.477	2.316	6.49	63.2
	AG4	2.455	2.290	6.71	66.4
BIT3	AG1	2.442	2.289	6.27	71.6
	AG2	2.650	2.473	6.68	60.9
	AG3	2.497	2.309	7.53	62.7
	AG4	2.446	2.279	6.83	68.4
BIT4	AG1	2.354	2.214	5.94	64.5
	AG2	2.502	2.347	6.21	72.3
	AG3	2.452	2.294	6.43	69.2
	AG4	2.354	2.211	6.08	63.6

$^{\xi}$ Average of five replicate specimens (diam 100 mm and height 100 mm) for each bitumen and aggregate.

subjected to moisture conditioning. This conditioning involved 3 hrs of vacuum saturation at 67 hPa pressure in distilled water to 55–80% saturation level, followed by 7 days of soaking at 40°C. The results of saturation level are listed in Table 2. All ten specimens were then cooled for 2 hrs at 10°C prior to testing for resilient modulus (ASTM D4123), followed by diametral split tensile strength (EN 12697-23:2003) at a similar temperature (10°C). The machine used was a servo-hydraulic testing system (MTS 810, Teststar II), and the order in which the runs were made was completely random to minimize bias.

To be sure that failure of the specimens was due to stripping, a close examination of the split failure surfaces (diametral planes) was made on each specimen. Stripping was clearly recognized, as some observable aggregate surfaces had lost bitumen, and no fracture surfaces or crushed aggregates were apparent. For the ten specimens from each bitumen/aggregate pair, retained strength defined as the ratio of mean strength of conditioned specimens, to the mean strength of dry specimens was used as a measure of stripping. Retained resilient modulus and tensile strength ratio (MRR and TSR, respectively) were used to measure water sensitivity of the interfacial bond. MRR or TSR value of 70% was taken as the minimum to ensure good performance, since it has been generally considered suitable by many agencies. For example, Lottman [14] and Tunnicliff et al. [15] recommended this value.

The variety and quantities of different compositions of the bitumens and aggregates would be expected to influence the sensitivity to moisture. With the four bitumens and four aggregates used, the data presented are from a total of sixteen different types of bituminous mixtures.

3. Results and discussion

The experimental results were evaluated with respect to the effect of (a) bitumen composition, and (b) aggregate composition on moisture sensitivity.

3.1. Bitumen composition

The chromatograms of the bitumens that were obtained from the GPC test are shown in Fig. 2a. Generally, all the bitumens seem to exhibit an early peak originating from large molecular size (LMS) eluting at about the same time, followed by a large, broad peak from small molecular size (SMS). The primary difference seems to be in the relative sizes of the peaks. Basing on these data, the bitumens are possibly qualitatively similar but quantitatively different. It is noticed that BIT1 has a small distinguishable shoulder on the major peak. Figure 2b presents the percent total areas under the LMS and the SMS peaks for the four bitumens. The results in the figure indicate some differences in the amounts of LMS and SMS.

From the infrared spectroscopy data, peaks of infrared absorbance in the region of 1710–1690 cm^{-1} corresponding to carbonyl stretch were used to characterize bitumen. This region is characteristic of functional groups like carboxylic acids, 2-quinolones, ketones and anhydrides, some of which could be crucial as regards moisture damage [5, 16]. To detect differences in the carbonyl part of the spectra studied in this work, the region was magnified on expanded abscissa as shown in Fig. 3. BIT3 particularly exhibits a prominent sharp peak around 1709 cm^{-1} for both ATR and ZnSe, while other bitumens show broad bands around this frequency.

To interprete the peaks around the carbonyl region, acid numbers for all the bitumens were determined in accordance with ASTM D 664-95, and

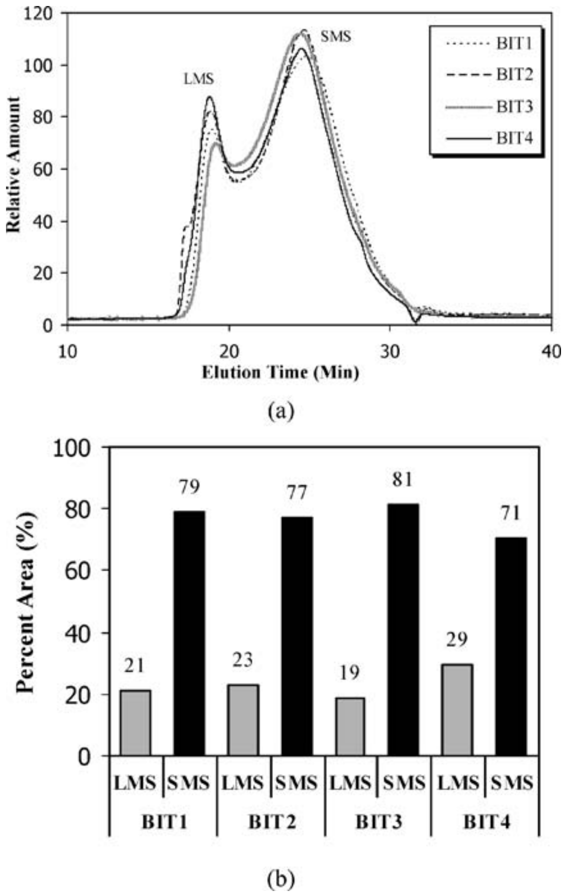

Fig. 2 Bitumen GPC results, (a) Size distributions, and (b) Areas under the peaks.

the data are given in Table 3. These data indicate that BIT3 possesses a significantly higher acid content than the other bitumens, at a 5% significance level. The absorbance levels for the bands between wavenumbers 1710 and 1690 cm^{-1} were calculated using the integrated peak area method with a computer program. The areas under absorbance spectra bands are proportional to concentrations of functional groups present in bitumen. Table 3 includes these areas for carbonyl bands of the four bitumens under study. These data indicate a good correlation between acid numbers and the integrated peak areas of the spectra (both ATR and ZnSe). Consequently, the observed peaks in the carbonyl region of the IR-spectra could be mainly due to bitumen acidic components. In this research, acid number was therefore used to represent the composition of the bitumen in terms of acidic components.

Table 3 Acid numbers and areas under IR-spectra of carbonyl region

Bitumen	Acid number (mg/g)*	IP$^{\beta}$ area for ATR spectra	IP$^{\beta}$ area for ZnSe spectra
BIT1	0.25	0.029	0.037
BIT2	0.48	0.079	0.104
BIT3	3.59	0.651	1.096
BIT4	0.52	0.086	0.141

*Means of two data values for each bitumen; $^{\beta}$ IP = Integrated Peak.

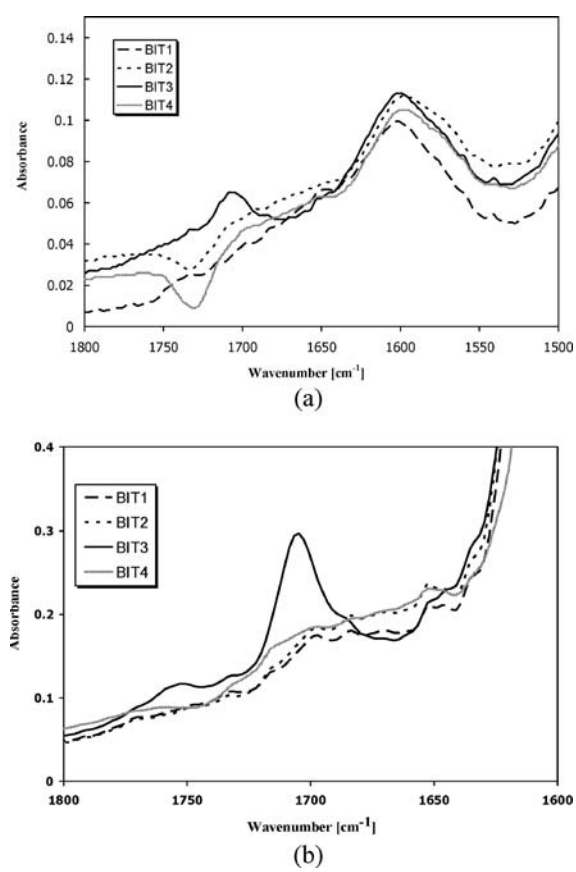

Fig. 3 IR spectra in the carbonyl region, (a) ATR Prism, and (b) ZnSe Cells.

3.2. Bitumen composition and mixture mechanical properties

The impact of bitumen composition on mixture mechanical properties was analyzed using bitumen acid numbers and grade (cf. Tables 1 and 3). Bitumen grade measures consistency, which relates to composition in terms of molecular size and associations due to polarity.

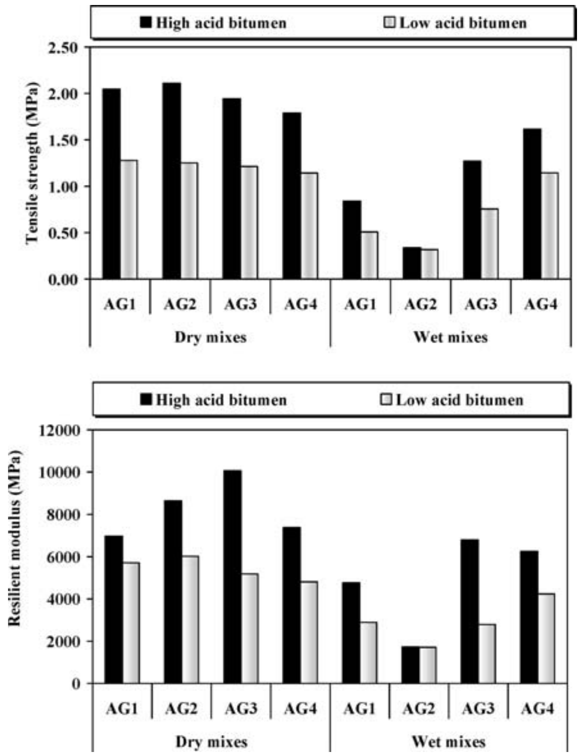

Fig. 4 Strengths data for the aggregates and two bitumens of different acidity.

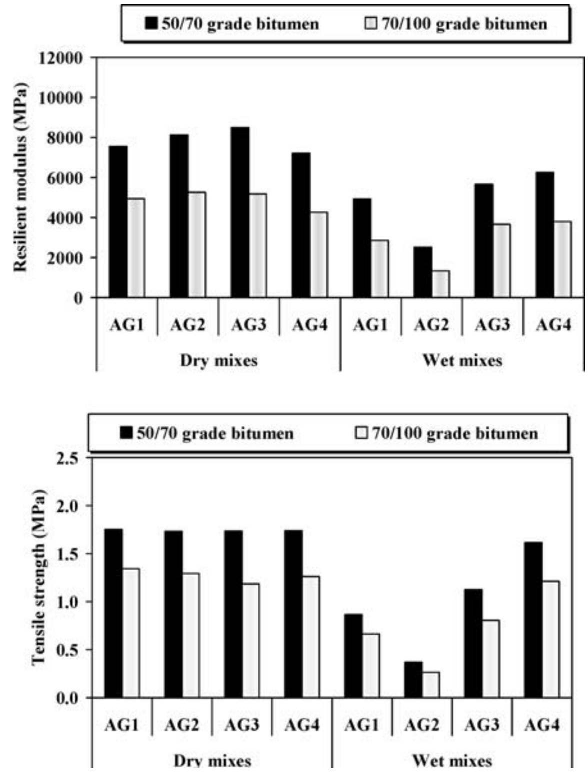

Fig. 5 Strengths data for the four aggregates and two bitumens of different grades.

In this study, mixture mechanical properties were represented by resilient modulus and tensile strength.

Determination of the effect of difference in bitumen acidity (given by acid number) on dry and wet mixture mechanical properties was done using two bitumens (BIT1 and BIT3). These bitumens were selected because of approximately similar penetration (cf. Table 1) and perhaps molecular size distribution (cf. Fig. 2b), but with a large difference in acid numbers. BIT1 exhibits a low acid number (0.25 mg/g), whereas BIT3 shows a high acid number of (3.59 mg/g, cf. Table 3). Figure 4 illustrates the dry/wet resilient modulus and tensile strength data for mixtures containing these two bitumens.

It can be observed that in general, mixtures from the high acidity bitumen exhibited higher resilient modulus and tensile strength than those from low acidity bitumen. However, in wet mixes, aggregate AG2 does not show a significant difference in resilient modulus and tensile strength. This finding suggests that, possibly, the effect of acidity on mixture mechanical properties in wet condition could be aggregate specific.

The impact of bitumen grade on dry/wet mixture mechanical properties was explored by using data on mixtures from bitumens BIT4 (grade 50/70) and BIT2 (grade 70/100), respectively. It should be noted that these two bitumens have almost similar acid numbers, and therefore, any observations on resilient modulus and tensile strength should not have any connection with change in acidity. Figure 5shows the dry/wet resilient modulus and tensile strength data from the two bitumens and all the four studied aggregates. In general, mixtures from the 50/70 grade bitumen show resilient modulus and tensile strength that are more than 30% higher compared to mixtures from the 70/100 grade bitumen. In other words, the grade of bitumen seems to affect the resilient modulus and the tensile strength of mixtures, in both dry and wet conditions. This trend is the same across all the studied aggregates. This could be due to strong association with aggregate surfaces because of higher concentration of the large sized and/or strongly polar interacting molecules in BIT4 compared to BIT2, as can be seen from the GPC results (cf. Fig. 2b). Plancher et al. [5] reported that large sized molecules in bitumen contain large aromatic ring systems. Such systems could supply polarizable π-electrons, which in turn coordinate with OH groups and other electron deficient centres of aggregate surfaces.

3.3. Statistical analysis of moisture sensitivity data

The MRR and TSR data were analyzed using statistical tools to evaluate moisture sensitivity. A test was made to establish if intervention via water conditioning influences the mechanical properties of the mixtures.

This was done by testing whether moisture sensitivity, as given by MRR or TSR, for bituminous mixtures from each bitumen/aggregate combination is significantly less than, equal to, or greater than 70%, respectively. For each of the five sample observations obtained in dry and wet conditions, respectively, sample means and estimates of standard deviation were used to evaluate moisture sensitivity.

Taking a threshold wet-to-dry strength ratio value of 70% (see section on testing programme), the formulation was such that the alternative hypothesis is two-sided. Analysis was done using a two-tailed t-test of the MRR and TSR data from all the mixture combinations. The decision criteria were formulated as shown in the upper part of Table 4. Three regions of the t-distribution were formed and arbitrarily named L, M or H, respectively, corresponding to the inference that MRR or TSR is significantly less than, equal to, or greater than 70%. The inferences drawn, based on the above criteria, are shown in the lower part of Table 4.

3.4. Effect of bitumen composition on moisture sensitivity

To study the impact of bitumen composition to moisture sensitivity, the MRR and TSR data for each aggregate and the four studied bitumens were arranged as shown in Table 5. As already mentioned, bitumen was

Table 4 Decision criteria and statistical inferences on MRR and TSR

Region	Condition	Decision	Inference
L	$t < -2.306$	Reject H_o	MRR or TSR < 70%: Mixture is sensitive to stripping
M	$-2.306 < t < 2.306$	Accept H_o	MRR or TSR = 70%: Mixture has average resistance
H	$t > 2.306$	Reject H_o	MRR or TSR > 70%: Mixture is resistant to stripping

			t-value for		Statistical Inference on wet-to-dry strength ratios					
					MRR (%)			TSR (%)		
Bitumen	Aggregate	$\lvert t_{8,0.025} \rvert$	MRR	TSR	H	M	L	H	M	L
AG1	BIT1	2.306	−4.514	−8.937			β			β
	BIT2	2.306	−3.112	−4.860			β			β
	BIT3	2.306	−0.298	−6.071		§				β
	BIT4	2.306	−3.009	−3.148			β			β
AG2	BIT1	2.306	−12.554	−8.078			β			β
	BIT2	2.306	−4.781	−7.822			β			β
	BIT3	2.306	−16.215	−20.660			β			β
	BIT4	2.306	−5.083	−5.152			β			β
AG3	BIT1	2.306	−6.202	−2.956			β			β
	BIT2	2.306	0.063	−0.233		§			§	
	BIT3	2.306	−0.513	−1.002		§			§	
	BIT4	2.306	−1.025	−1.119		§			§	
AG4	BIT1	2.306	2.614	5.504	x			x		
	BIT2	2.306	5.121	6.734	x			x		
	BIT3	2.306	2.235	3.718		§		x		
	BIT4	2.306	5.634	6.865	x			x		

x = mixture with high resistance to moisture, §= mixtures with medium resistance, and β = mixture sensitive to moisture

Table 5 Moisture sensitivity of mixtures and bitumen characteristics

Aggregate	Bitumen	Damage ratios (%)		Bitumen Characteristics		
		MRR	TSR	Acid No. (mg/g)	Grade	LMS area (%)*
AG1	BIT1	50.7	39.7	0.25	70/100	21
	BIT2	57.8	49.4	0.48	70/100	23
	BIT3	68.4	41.1	3.59	70/100	19
	BIT4	55.3	49.4	0.52	50/70	29
AG2	BIT1	26.8	22.2	0.25	70/100	21
	BIT2	25.4	20.4	0.48	70/100	23
	BIT3	20.1	16.0	3.59	70/100	19
	BIT4	30.9	21.3	0.52	50/70	29
AG3	BIT1	53.7	62.3	0.25	70/100	21
	BIT2	70.7	68.0	0.48	70/100	23
	BIT3	69.5	65.5	3.59	70/100	19
	BIT4	66.6	64.9	0.52	50/70	29
AG4	BIT1	88.1	100.2	0.25	70/100	21
	BIT2	89.3	96.0	0.48	70/100	23
	BIT3	84.6	90.3	3.59	70/100	19
	BIT4	86.7	92.9	0.52	50/70	29

*This is the percent area under the large molecular size peak from GPC (cf. Fig. 2b)

characterized using acid number (representing acidic components), bitumen grade (representing binder consistency), and LMS area from GPC (representing relative distributions of molecular sizes and/or associations, cf. Fig. 2 and Table 5).

Generally, across the four bitumens, the MRR and TSR data do not seem to indicate any significant variation in moisture sensitivity for a particular aggregate. For example, data in Tables 4 and 5 indicate that the most moisture sensitive mixtures (corresponding to aggregate AG2) exhibit almost similar values of MRR and TSR across all studied bitumens. This observation is apparent, despite the differences in acid numbers (e.g. BIT1 and BIT3), penetration grading (e.g. BIT2 and BIT4) and molecular size distribution (e.g. BIT3 and BIT4). The same observation was made for low moisture sensitivity mixtures, corresponding to aggregate AG4, and indeed all other aggregates, as given in Table 5. Consequently, based on the results of this study, there appears to be no obvious pattern relating bitumen characteristics as acid number, penetration grade and molecular size distribution and moisture sensitivity of bituminous mixtures. However, it can be noted from Table 4 that for aggregate AG3, bitumen BIT1 exhibited moisture sensitive mixtures, contrary to the other three bitumens. The MRR and TSR values were approximately 54 and 62%, respectively, and were both significantly less than 70%, as seen from the same table. The reason for this apparent anomaly could not be found from the results of this study.

3.5. Aggregate composition

The composition data of the aggregates, based on chemistry and mineralogy, are listed in Table 6. It can be seen that the aggregates are diverse with respect to chemical and mineralogical composition. For instance, aggregate AG4 shows a high composition of SiO_2 (90%) and quartz (99%) compared to the rest of the aggregates. Aggregates AG1 and AG3 contain comparatively high lime feldspar content (42 and 54%, respectively), while AG2 contains a higher alkali feldspar content (53%), in comparison with the other aggregates. Differences can also be observed in the amounts of iron, sodium, potassium and calcium, contained in the four aggregates. These elements have been reported to influence adsorption of bitumen components onto aggregate surfaces [9].

3.6. Aggregate composition and mixture mechanical properties

The resilient modulus and tensile strength data of all the mixture combinations, both before and after conditioning, are given in Fig. 6. The coefficients of variation for the different random 5-sized samples

Table 6 Composition data of the aggregates used in this study

	Chemical Composition (% Weight)							
Aggregate	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe oxide	MnO_2
AG1	71.2	18.0	6.30	0.30	0.82	1.70	1.61	0.06
AG2	71.9	15.4	1.64	1.14	2.70	5.35	1.80	0.11
AG3	53.7	22.4	8.10	0.54	2.80	1.64	10.63	0.20
AG4	89.5	9.3	0.04	0.06	0.06	0.40	0.64	0.04
		Mineralogical composition (%)						
	Rock Name	Quartz	Alkalifeldspar	Limefeldspar	Ferro magnesian	Others		
AG1	Granite	42	10	42	ND	7		
AG2	Syeno-granite	27	53	13	ND	7		
AG3	Tonalite	18	4	54	19	6		
AG4	Quartzite	99	ND	ND	ND	Trace		

ND = Not Detected

tested were less than 10% in almost all cases. Also shown in the figure are 95% confidence limits for each set of the 5-sized random samples (both dry and conditioned) plotted as error bars. Generally, the variation seems to be low, indicating a good repeatability of the data.

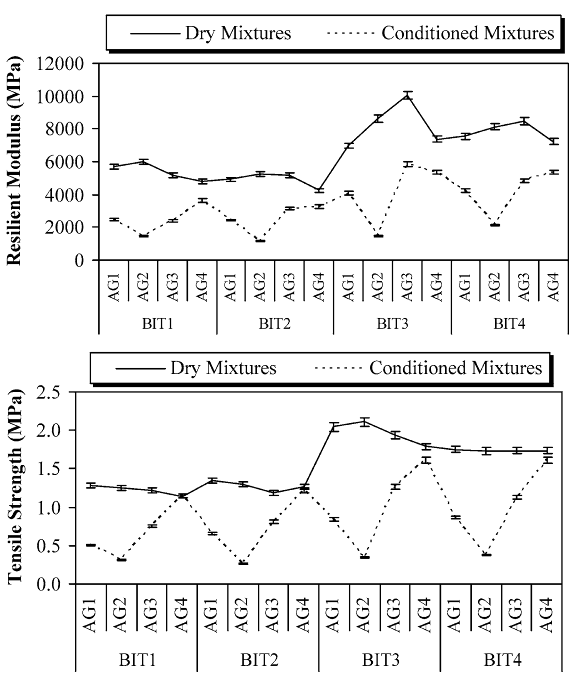

Fig. 6 Resilient modulus and tensile strength data for the mixtures.

From the plots, it is observed that the highest *dry strengths*, as given by resilient modulus and tensile strength, seem to be associated with BIT3, and in particular aggregates AG2 and AG3. This outcome could be attributed to the relatively high concentration of acidic components (high acid number) that adsorb onto aggregate surfaces. This observation agrees reasonably well with findings from fundamental studies by Plancher et al. [5] and Petersen et al. [7]. BIT4 also seems to have a relatively high dry resilient modulus and tensile strength compared to BIT1 and BIT2 for all aggregates studied. This observation is perhaps due to the lower penetration grade exhibited by this bitumen.

In general, there seems to be little variation in *dry strength* with change in aggregate for each of the studied bitumens although the dry resilient modulus for AG3 seems to be about 70% higher than that of AG1 for the highly acidic BIT3. On the other hand, generally, variability in *wet strength* with aggregate, for the same bitumen, seems to be significant. For all the bitumens, aggregate AG2 exhibited the lowest *wet strength* basing on both resilient modulus and tensile strength (cf. Fig. 6). This aggregate contains comparably high contents of total acid insolubles (87%), alkali metals in its oxides (8% total) and alkali feldspars (53%), as given in Table 6. Alkali metals probably contribute to formation of salts, which are relatively water soluble.

The relatively high *wet strengths* for aggregates AG1 and AG3 could be explained by the presence of lime feldspars (42 and 54%, respectively; cf. Table 6), that

Table 7 Moisture sensitivity of mixtures and aggregate characteristics

		Moisture Damage Ratios (%)				Aggregate Mineral content(%)		
Bitumen	Aggregate	MRR	Rank$^{\omega}$	TSR	Rank$^{\omega}$	Quartz	Alkali feldspar	Lime feldspar
BIT1	AG1	50.7	(3)	39.7	(3)	42	10	42
	AG2	26.8	(4)	22.2	(4)	27	53	13
	AG3	53.7	(2)	62.3	(2)	18	4	54
	AG4	88.1	(1)	100	(1)	99	ND	ND
BIT2	AG1	57.8	(3)	49.4	(3)	42	10	42
	AG2	25.4	(4)	20.4	(4)	27	53	13
	AG3	70.7	(2)	68.0	(2)	18	4	54
	AG4	89.3	(1)	96.0	(1)	99	ND	ND
BIT3	AG1	68.4	(3)	41.1	(3)	42	10	42
	AG2	20.1	(4)	16.0	(4)	27	53	13
	AG3	69.5	(2)	65.5	(2)	18	4	54
	AG4	84.6	(1)	90.3	(1)	99	ND	ND
BIT4	AG1	55.3	(3)	49.4	(3)	42	10	42
	AG2	30.9	(4)	21.3	(4)	27	53	13
	AG3	66.6	(2)	64.9	(2)	18	4	54
	AG4	86.7	(1)	92.9	(1)	99	ND	ND

ND = Not Detected; $^{\omega}$rank of MRR or TSR for aggregates mixed with a particular bitumen.

have calcium at their mobile sites. Aggregate AG3 also contains ferromagnesian (19%, cf. Table 6), which has calcium, magnesium and iron. In fact, the chemical composition data in Table 6 indicate high concentrations of iron and calcium (11 and 8%, respectively) for aggregate AG3. After interacting with bitumen acidic components, calcium, iron and magnesium seem to form acid salts, which are comparably water-stable. Essentially, aggregates AG1 and AG3, mixed with the most acidic bitumen, BIT3, exhibited very high wet resilient modulus and relatively high wet tensile strength (cf. Fig. 6).

Mixtures from aggregate AG4 showed high values of resilient modulus and tensile strength, both in dry and wet conditions. Specifically, the high values of wet resilient modulus and wet tensile strength across the studied bitumens were amazing, as several studies found in the literature indicate that this type of aggregate (a quartzite) is considered to be rather water sensitive. The reason for this discrepancy could not be discerned from this work.

3.7. Aggregate composition and moisture sensitivity

The dependency of moisture sensitivity on aggregate composition was evaluated. The moisture sensitivity data (as given by MRR and TSR) were grouped by aggregate type for every bitumen as shown in Table 7.

For each bitumen, the four aggregates were ranked in such a manner that the highest rank (i.e. one) was given to the aggregate with the lowest moisture sensitivity. The ranks are shown in parentheses adjacent to each value of MRR or TSR. Table 7 also lists the mineralogical composition data (from Table 6) in terms of contents of quartz, alkali feldspars and lime feldspars (mainly plagioclase) contained in each of the aggregates.

The MRR and TSR data in Table 7 indicate that, in general, mixtures from aggregate AG4 exhibited the highest rank, followed by AG3, AG1 and AG2, respectively. This is apparent, irrespective of the bitumen used. Furthermore, the data indicate that the moisture sensitivity ratios based on resilient modulus and indirect tensile tests, respectively, are well correlated in the ranking.

The statistical analysis done in Section 3.3 (cf. Table 4) indicates that AG2 exhibited the highest sensitivity to moisture. As shown in Table 4, aggregate AG2 contains some quartz (27%) and mainly alkali feldspars (53%, both Orthoclase – $KAlSi_3O_8$ and Albite - $NaAlSi_3O_8$). The total acid insoluble content is very high (87%, cf. Table 4) with largest contribution from SiO_2 (72%). The corresponding contents of CaO, MgO and Fe-oxide were low. The relatively high contents of alkali metals (Na and K) most likely contribute to the high moisture sensitivity. The alkali metals possibly form monovalent cation salts of acids, which could be easily removed from the aggregate surface by water.

Aggregate AG3 was ranked second for all the studied bitumens, as shown in Table 7, and the statistical analysis (cf. Table 4) indicates that this aggregate exhibited average stripping resistance for bitumens BIT2, BIT3 and BIT4, and high moisture sensitivity with bitumen BIT1, which in fact has the lowest acid number (cf. Table 3). Aggregate AG3 contains lime feldspars (54%), quartz (18%) and ferromagnesian $(Ca,Mg,Fe)(Si,Al)_2O_6$ (19%), as given in Table 6. The data in the table reveals that it contains about 8% of CaO and 11% of Fe-oxide. The presence of calcium and iron could be one reason behind the generally observed intermediate resistance to moisture damage.

The data in Tables 4 and 7 indicate that mixtures from aggregate AG1 (third in rank) and all the studied bitumens showed high moisture sensitivity. The level of total acid insolubles in aggregate AG1 is about 89% (cf. Table 6). The aggregate contains 42% quartz, 10% alkali feldspars, and 42% lime feldspars, as shown in Table 6. It can be noted that the MRR value for mixtures made with aggregate AG1 and bitumen BIT3 exhibit average resistance to stripping, although the TSR reflects low resistance.

Mixtures from aggregate AG4 exhibited the lowest moisture sensitivity for the studied bitumens. This aggregate is a quartzite with practically 100% quartz, as shown in Table 6. As noted earlier (cf. Section 3.6), a reasonable explanation for this observation could not be found from the results of this study.

4. Factorial analysis

To augment the foregoing discussion, the MRR and TSR data were analyzed after arranging them as a two-factor design without replication. The intent of the analysis was to check whether moisture sensitivity, as given by MRR and TSR values, is affected by bitumen and aggregate, and possibly their interaction. Since the data did not have replicates, interaction was examined using the Tukey test [17], which employs a regression approach and tests for non-additivity, rather than data replicates that would provide the required degrees of freedom.

An analysis of variance (ANOVA) was done on the data to determine if, for a particular bitumen, at least two of MRR or TSR treatment means were different at a 0.05 level of significance, with aggregate as the treatment. The same analysis was done for a particular aggregate by taking bitumen as the treatment. The p-values and F-statistics obtained from ANOVA are shown in Table 8. These results indicate that for both moisture damage ratios (MRR and TSR), bitumen type is not significant ($p > 0.05$) while aggregate is highly significant ($p \ll 0.05$). The R^2 values for MRR and TSR were 96 and 99%, respectively. Consequently, the results from this analysis indicate that more than 95% percent of variability in the moisture sensitivity is attributed to aggregate. There is no statistical evidence, based on this analysis, to support the assertion that the bitumens used in this study affect moisture sensitivity of mixtures.

Table 8 P-values and F-values extracted from the ANOVA results

	MRR		TSR	
Factor	p-value	F-value	p-value	F-value
Bitumen	0.093	2.91	0.297	1.43
Aggregate	1.18×10^{-6}	73.6	2.53×10^{-9}	298.3

The results of the statistical analysis using the Tukey test indicated no evidence of interaction effect between bitumen and aggregate on MRR as well as TSR. A pairwise comparison between individual means of response values was made to discover specific differences in aggregates. Duncan's multiple range test was applied to the means of MRR and TSR for the different aggregates. The mean square error was used as the best estimate of the experimental error variance. The outcome of the data analysis indicated that all pairs of aggregates are significantly different.

Although the correlation between the moisture damage ratios was good, TSR has been shown to suffer from repeatability problems, especially when assessing the effectiveness of antistripping additives.

5. Conclusions

The results presented in this paper led to the following conclusions:

(a) Mechanical properties of mixtures like resilient modulus and tensile strength in dry condition were generally sensitive to acidity and grade of the bitumens used in this study. The bitumen with highest acid number, as well as the one with lower penetration grade, exhibited comparably high mechanical properties in dry condition. However, in the wet condition, the influence of bitumen acidity on resilient modulus and tensile strength were aggregate specific.

(b) For each of the studied aggregates used in bituminous mixtures tested, bitumen characteristics like acid number, penetration grade and molecular size distribution did not influence moisture sensitivity of mixtures.

(c) For each of the studied bitumens, resilient modulus and tensile strength in the dry condition were not influenced by aggregate. However, in wet conditions, the aggregate containing high contents of alkali feldspars and low calcium, magnesium and iron were associated with mixtures that exhibited reduced strength. One aggregate with practically 100% quartz exhibited low moisture sensitivity contrary to findings in the literature.

(d) The results indicated that mixtures from aggregates containing alkali metals like sodium and potassium exhibit relatively high moisture sensitivity, irrespective of the bitumen used. On the other hand, there were no indications of moisture sensitivity (MRR and TSR values were $\geq$70%) in aggregates with calcium, magnesium and iron.

(e) The results revealed a good correlation between moisture sensitivity ratios based on resilient modulus and tensile strength in ranking mixtures for moisture sensitivity.

(f) Statistical analysis showed that variability in moisture sensitivity data of mixtures tested may be attributed to aggregate rather than bitumen. In addition, there was no significant interaction effect between bitumen and aggregate, on moisture sensitivity.

(g) Additional research is required to correlate the findings of this work with trial sections made using the studied materials, and extended to a wider combination of diverse bitumen/aggregates.

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