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Laboratory studies on stripping at bitumen/substrate interfaces using FTIR-ATR

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Abstract A technique based on Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR) was developed and used to study movement of water into bitumen/substrate interfaces, as well as to characterize stripping. Bitumens from different sources were used and applied on various substrates (silicon, germanium and zinc selenide) as thin films. The influence of bitumen type, substrate type, temperature, film thickness and modification with amines, on water damage was studied. The technique gave information on water flow into interfaces and how stripping possibly occurs. It distinguished between stripping and non-stripping bitumens. At least one of three processes occurred, namely water diffusion, film fracture, and bitumen displacement by water, respectively. The diffusion of water did not obey Fick's law. Stripping was influenced by bitumen source when silicon and germanium substrates were used. Notching the films made the process of water entry almost occur immediately. Additives significantly reduced stripping in the moisture-sensitive bitumen on silicon and germanium substrates, even after film notching. Although, good agreement was observed between tests for the bitumens that did not strip, the tests on stripping bitumens showed poor agreement.

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Introduction

In bituminous mixtures, proper adhesion of the bitumen onto aggregate surfaces is a pre-requisite to guarantee good performance. Moisture damage mainly occurs in bituminous mixtures due to loss of adhesion between the bitumen and aggregate surfaces, a process commonly called stripping. This phenomenon is linked to complex combinations of bitumen and aggregate properties.

The fundamental physicochemical mechanisms behind movement of water to the interface and how it competes with bitumen to cause its removal from the aggregate surface are not fully understood. A review of literature indicates several mechanisms proposed to explain the stripping process. These mechanisms include displacement, detachment, spontaneous emulsification, film rupture, hydraulic scouring, and others. Irrespective of the mechanism(s) present, there appears to be initiation and progression of stripping culminating in removal of bitumen from the aggregate. Central to the mechanisms mentioned, some important questions arise like:

- What pathway does water follow when moving from the environment into the interfacial region?
- What is the characteristic behavior of removal of bitumen from the surface by interfacial water?

The study reported in this paper was aimed at developing a measurement method based on FTIR-ATR spectroscopy that can be used to evaluate transport of water into bitumen/aggregate interfaces via bitumen films, and check whether the method can successfully be used to characterize stripping at the interface. The method was applied using thin bitumen films put on crystal substrates and letting water move through the films towards the bitumen/substrate interfaces. In addition, the above systems were perturbed by factors such as the film thickness, temperature, bitumen modification, nature of substrate and bitumen penetration grade to evaluate their individual effects on the mechanisms under study.

Review of relevant literature

This section provides information that is considered relevant to the studies reported in this paper.

Interfacial adhesion between bitumen and aggregate surfaces is important for proper performance of bituminous pavements. When bituminous mixtures are exposed to water, bitumen can be displaced from the aggregate because water breaks interfacial adhesive bonds between the two materials. This phenomenon, commonly known as stripping, has been the subject of great scientific interest for quite some time as evidenced by numerous publications. Most literature links stripping to several variables like bitumen and aggregate properties, hot mix processing, quality control during construction, dynamic effect of traffic loading, type and properties of anti-stripping additives, and others. For a detailed review of fundamentals on these aspects, the reader is referred to [1–3].

It is not yet well known how exactly water enters the bitumen/aggregate interface. In addition, the process of stripping is not clearly characterized fundamentally. The mechanisms proposed in literature to explain stripping are still speculative and most of them have not been reliably proved through laboratory experiments. These mechanisms include displacement of bitumen by water along the aggregate surface, detachment of bitumen films from the aggregate surface due to a build-up of water at the interface, spontaneous emulsification due to formation of an inverted water-in-bitumen emulsion, film rupture due to excessive pore water pressure, and others.

When water enters the interface, it tends to wet many aggregate surfaces. Previous fundamental studies [4, 5] indicate that some aggregates show preference for water compared to bitumen. For example, siliceous surfaces have surface hydroxyl groups that interact with water through stronger hydrogen bonds than they do with bitumen components, since the latter are less polar than water. Carboxylic acids in bitumen have, for instance, been shown to be readily desorbed from aggregate surfaces by water even though they strongly adsorb in dry conditions. On the contrary, other bitumen components like pyridines are not easily replaced by water [5]. This indicates that characteristic behavior of the process of bitumen removal is dependent on both the bitumen and aggregate sources.

To the authors' knowledge, the only study on flow of water across bitumen films was conducted by Nguyen et al. [6] as part of the SHRP project. Nguyen and co-workers studied the transport properties of water through asphalt layers by using FTIR-ATR involving five SHRP asphalts and a model siliceous substrate. They detected and quantified water at or near the interfaces of these materials. Their results indicated that water moves across bitumen films by diffusion. However, reliability of their method seems to be questionable due to several drawbacks like:

- The assumption of Fickian diffusion, that may not be correct because water and bitumen are incompatible and at steady state, water concentration cannot be uniform across the bitumen film,
- They used an indirect method of asphalt thickness measurement, which could reduce accuracy of the results,
- Capillary attraction at the edges may have caused a change in uniformity of bitumen film thickness,
- Water was constantly moving through the water chamber and this would somewhat influence how it flows across the bitumen films,
- Their conditioning chamber gave full saturation which does not exactly simulate the conditions in the field, and
- Repeatability of their method was not established.

Karlsson and Isacsson [7] applied the principle of FTIR-ATR in studying diffusion of rejuvenators into bitumen films. The method was versatile and could be used to examine the influence of other parameters like temperature, bitumen type and film thickness.

In the study reported in this paper, modifications were made to the method and subsequently used to study water transport into the interfacial region across bitumen films, as well as to characterize stripping of bitumen from substrate surfaces by water.

Experimental

Materials selection

The different bitumens used in this study and some of their details are listed in Table 1. They were selected based on their wide differences in source, acidity and penetration grade. Furthermore, two commercial liquid anti-stripping additives (Duomeen and Redicote) were used. The additives were supplied by Akzo Nobel,

Table 1 Details of bitumens used in this investigation

Bitumen	Origin	Pen grades*	Total acid number#
Laguna B60	Laguna, Venezuela	50/70	–
Laguna B85	Laguna, Venezuela	70/100	3.6
Laguna B180	Laguna, Venezuela	160/220	3.9
Laguna B370	Laguna, Venezuela	320/400	–
Mexican B180	Mexico	160/220	0.1
Arabian B180	Middle east	160/220	0.1

* Numbers indicate penetration at 25 °C in dmm according to EN 12591

Tested according to ASTM D 664

Sweden. Supplier information indicated that the additives are multi-component materials. Duomeen was a fatty diamine with the main component being *N*-oleyl-1,3-diaminopropane and Redicote was mainly a fatty imidazoline. In modifying the bitumens, the anti-stripping additives were mixed with bitumen by carefully adding the required weight (0.5% w/w) to hot bitumen that had been oven-preheated for 3 h at 100 °C in metallic cans. The additive and bitumen were then mixed by stirring continuously for 5 min using a warm spatula. The cans containing the blends were sealed and placed at room temperature awaiting the time for testing.

Thin oblong trapezoidal (72 × 10 × 6 mm) non-absorbing spectroscopic grade, 45° ATR crystals of zinc selenide (ZnSe), silicon (Si) and germanium (Ge) with flat top faces were employed in this study. At 45° angle of incidence, this size of prism gives six reflections, which provide a reasonable path length for creating good intensity of the resulting beam. The prism surfaces were used as received without any modifications.

Developed test procedure

Theory of FTIR-ATR

Since the method developed was based on FTIR-ATR, a brief review of its underlying theory is made. Attenuated total reflectance (ATR) is a versatile reflection spectroscopic technique. When infrared light is directed through an ATR prism, it undergoes multiple total internal reflections owing to the reflection angle being greater than some critical value. The boundary conditions at the reflecting surface cannot be satisfied with only the incident and reflected beams of radiation. As a consequence, some radiation, commonly called an evanescent wave, penetrates the sample placed on the prism and its intensity decreases exponentially with distance from the surface of the prism. The penetration depth is the distance at which the amplitude of this wave reduces to 37% of its original value. The penetration depth of this evanescent wave is a function of the angle of incidence, wavelength of the radiation and the refractive indices of the substrate and the sample.

When a bitumen film is exposed to an aqueous environment, water can enter the interface via the film and interact with the evanescent wave and hence be detected. The emerging beam out of the prism is attenuated owing to absorption by water reaching the reflecting surface and other molecules present. As a consequence, an infrared spectrum yielded shows presence of water at the interface. The amount of water detected is proportional to the area under the absorption band corresponding to OH stretch vibrations. An example of an absorption spectrum of pure water on a zinc selenide crystal is shown in Fig. 1a. For the absorption spectra of the thin bitumen film samples exposed to water, the intensities of the bands around 3400 and 1640 cm^{-1} characteristic of OH stretch and bend, respectively, should increase as the interface gets enriched with water as depicted in Fig. 1b. The latter band is insensitive to low water concentrations and was not used in this study. The negative band around 2920 cm^{-1} is ascribed to bitumen. This band decreases with exposure time as the water displaces the bitumen film from the prism surface. The internal reflection

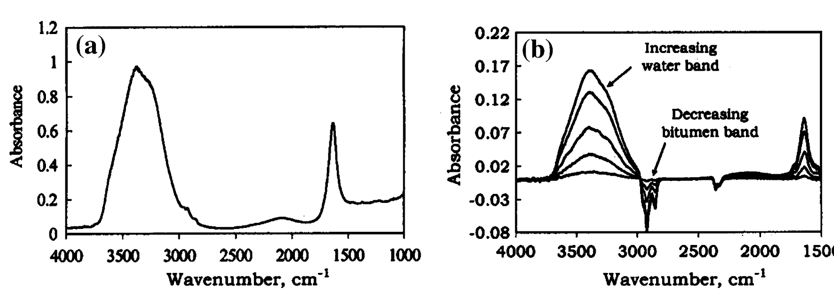

Fig. 1 Absorption spectra for (**a**) pure liquid water (**b**) water exposed films, after correction for background absorption

element is made of material with a higher refractive index than the sample under investigation. Examples of such materials include zinc selenide (ZnSe), silicon (Si), germanium (Ge) and diamond (C).

Detailed description of the method

In the proposed set up used in this study, two thin brass frames of thickness 200 μm were fixed on top of the ATR prism using hydrophobic adhesive glue. The upper frame had a bigger slot (68 by 6 mm) than that of the lower one (67 by 5 mm). The prism with the glued frames was tightly fixed into the sample compartment of the spectrometer by gluing ensuring no leakage. This was done to ensure that the only pathway for water into the interface was through the bitumen film in the slot. Figure 2 shows a schematic of the method setup.

The top face of the prism was cleaned with a soft napkin soaked in acetone and left to dry. The sample chamber was fixed into the spectrometer so that the top face of the prism was horizontal. A small sausage-like sample of bitumen was carefully applied onto the face of the prism within the slot of the brass frame (typically at room temperature). The temperature was then set to 80 °C and the bitumen left for a minimum of 1 h to melt and completely fill into the brass frame slot, hence establishing good initial contact with the whole face of the prism. This would also prevent the problem of pinholes or air bubbles in the bitumen film that might provide pathways for water, as well as interact with the evanescent wave. To prepare 200 μm bitumen films, a heated metallic scraper that would just fit into the slot of the upper frame was used to trim the bitumen to the final thickness. For 400 μm bitumen films, a wider scraper was used ensuring that bitumen would fill the slots of both the upper and lower brass frames. These thickness values are far greater than the penetration depth of the evanescent wave. The temperature was set to the required value to be maintained throughout the experiment.

A Mattson Infinity series 60 AR spectrometer fitted with an automatic temperature recorder (GRASEBY SPECAC) heatable to 200 °C was used. When temperature was within 1 °C of the set value, data acquisition commenced by taking a background scan. This spectrum allows corrections for differences in each prism used, and for varying atmospheric conditions inside the instrument. The resolution was set at 4 cm^{-1} and scans saved as interferograms for every minute (64 scans per minute) throughout a spectral bandwidth specific for a particular prism (e.g. 4000–1200 cm^{-1} for the silicon prism) and the iris was set to 100%. The computer was programmed to collect a total of 999 files with one file collected every 1.23 min. To reduce variability in the time of onset of the stripping phase, bitumen films were notched as part of this study. A notch with dimensions 10 mm long by 0.7 mm wide was made in the intact thin bitumen film on the prism by use of a sharp plastic screw-driver. The long axis of the notch was always made parallel to the long axis of the crystal. By notching the bitumen film, the commencement of an eventual stripping phase was controlled (See results section for more details).

The computer program was started and the interferograms immediately begun to be recorded. When 50% of the scans were finished, the lower trough of the sample compartment was slowly and carefully filled with distilled water until it just filled without excess water into the larger basin (cf. Fig. 2). By this time, temperature had reached the set value and was fairly uniform throughout the sample. The top boundary of the sample holder was first fitted with a water-tight cushion and then a hard plastic cover finally placed with two 100-g weights on top to ensure that no water leaks to the environment. A uniform temperature in the sample environment was guaranteed by placing an insulating cup over the whole assembly during the experiment. A macro was developed to automatically process the interferograms and the background file into difference absorbance diagrams, which were also saved. The net absorbance for each file was obtained by the peak height method between 3965 and 2800 cm^{-1} as

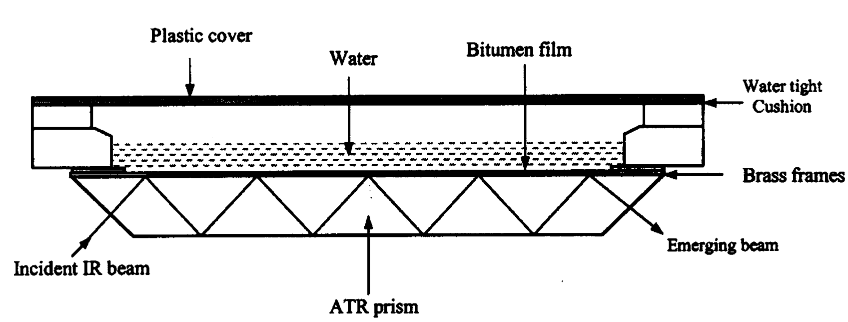

Fig. 2 Schematic of a section through the set up for FTIR-ATR testing

baseline ends, and 3431 cm^{-1} as the peak. This band is attributable to OH stretch in the water molecules. The calculated absorbance data were transferred into a spreadsheet for analysis.

Parameters examined

Several parameters were examined in evaluating the suitability of this procedure to quantify water at the bitumen/substrate interface namely (1) source and grade of bitumen, (2) nature of substrate by using different crystals (mainly Si and ZnSe, as well as a limited number of tests with Ge), (3) bitumen modification using liquid additives (Duomeen and Redicote), (4) testing temperatures (50 and 60 °C), and (5) whether the bitumen film was notched or intact. In this study, the bitumens were coded for ease of reporting the results. *L*aguna, *A*rabian and *M*exican bitumens were denoted L, A and M, respectively. In addition, a number attached to their code corresponds to the nominal penetration grade. For example, L180 is Laguna bitumen with nominal penetration grade of 180.

Results

To assess the test method described in the preceding section, and possibly indicate its relevance to other fields, a number of tests were performed. Difference spectra obtained for the various samples were used to calculate the intensity of water absorption.

Processing of the data

In this study, the amount of water detected at the interface through spectroscopic measurement was considered to be a measure of stripping propensity between bitumen and substrate material. Plots of absorbance (peak height) against time were used to study the rate of entry and amount of water detected within the depth of penetration of the evanescent wave. Generally, the results obtained indicated that during the experiment, the intensity of the water OH stretch bands examined increased with time of exposure. For some bitumens, the absorbance-time plots indicated a tendency for diffusion of some water across bitumen films. Attempts to fit the theoretical diffusion equation (Fick's 2nd law) to these data did not yield good fits. For other bitumens, the plots indicated that depending on the bitumen used, at least one of three phases are experienced during water-induced damage in the bitumen film and the interfacial region. These phases given in order of occurrence include

1. Diffusion involving flow of water from the environment into the interface across an intact bitumen film,
2. Sudden fracture of the bitumen film leading to high rate of water entry into the interface as depicted by the rapid increase in absorbance, and
3. Displacement of bitumen from the substrate surface by water.

Figure 3 illustrates these three damage phases for the Laguna 180 pen grade bitumen tested at 60 °C on the silicon crystal, where the three phases were all exhibited. Some of the bitumens tested did not exhibit all these phases. As seen from the figure, there seems to be diffusion for about 90 min after which a sudden increase in water absorbance takes place. In some cases, the occurrence of phase 2 was observed immediately the test begun, especially after notching the films. The bitumens that did not show stripping exhibited only the first phase.

In this study, two parameters were chosen to characterize stripping in the interfacial region between the bitumen and the substrates. The first one is the slope of the curve in phase 2, where the rate of change of absorbance ($S_A = \Delta A/\Delta t$) is noticed to be high (cf. Fig. 3). The time at which this phase begins seems to be random in the case of intact bitumen films, as it was observed to change with the same samples tested many times under similar conditions. The second parameter is the ratio of the final absorbance (A_f) to the maximum infrared absorbance of pure liquid water (A_w) for film free substrates obtained from Fig. 1a. This ratio (denoted by $D_R = A_f/A_w$ in this study) is reported as a percentage, and it gives the proportion of the crystal surface that has been stripped. It is noted that the intensity of the ATR spectrum is related to the penetration depth of the evanescent wave in the sample. Since the penetration depth is dependent on the refractive index of the crystal, among other things, the value of A_w is substrate crystal specific. The measured mean values of A_w obtained for zinc

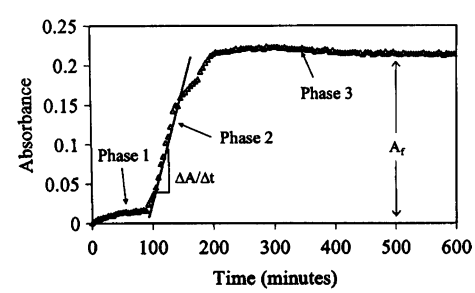

Fig. 3 Absorbance of Laguna 180 pen grade bitumen at 60 °C on the silicon crystal

selenide, silicon and germanium crystals using pure liquid water on the crystal surface were 0.798, 0.363 and 0.234, respectively. These are the values that were used to compute D_R for the respective crystals.

Influence of different factors

Results obtained using silicon crystal

Table 2 shows the values of parameters S_A and D_R for silicon crystal, when bitumen films exposed to water were tested at different temperatures. Results for both intact and notched films are given. It also includes information on the visual rating that was done basing on the perception of the researchers by looking at the extent of the displacement of bitumen from the crystal surface after each experiment. Modification was done for Laguna and Arabian bitumens by mixing them with Duomeen and Redicote to check whether these additives reduce the parameters S_A and D_R.

The results indicate that the highest damage was exhibited by Laguna bitumen. The results also indicate that, in general, the damage parameters for Arabian and Mexican bitumens are almost similar to but lower than those of Laguna bitumen, although the notched Mexican bitumen showed higher damage than the notched Arabian bitumen all tested at 60 °C. Results for acid number showed that Laguna bitumen contains high acid content (cf. Table 1). This leads to the belief that acid content is possibly one of the factors with a major influence on the moisture damage observed. This observation is supported by work conducted by Plancher et al. [4] and reported in AAPT, vol. 46, 151–175, 1977, where they reported that acids readily adsorb on aggregate surfaces but are easily displaced by water.

For all the 180 pen grade bitumens tested on the silicon substrate, the results show a decline in the damage parameters as the temperature decreases from 60 to 50 °C. The decrease seems to be greater in the intact bitumen films compared to the notched ones. For example, when the temperature drops from 60 to 50 °C, the decrease in D_R for the Laguna bitumen is 60% when the film is intact. The corresponding decrease in the notched film is 21%.

There seems to be an immediate commencement of water entry into interfaces when the bitumen films are notched (cf. Fig. 4). When a notch is created, the stripping process is evoked at interfaces of the bitumens, since water immediately gets in contact with the crystal surface at the point where the notch is located. For bitumens where the substrates prefer water to the bitumen, displacement of bitumen by water seems to occur at a higher rate. The rate of water entry into the interface and the extent of damage both seem to be bitumen specific as seen in Fig. 4. For instance, for the notched films, the highest damage was exhibited by Laguna (L180) followed by Mexican bitumen (M180) and lastly the Arabian bitumen (A180), which did not show stripping. In cases of intact bitumen films, stripping did not seem to always begin immediately (cf. Fig. 4).

The influence of adding liquid amines to the bitumens can be seen from the results in Table 2 and Fig. 5. The results in Table 2 indicate a drop in the damage parameters after modifying the bitumens with 0.5% of the liquid additives. Specifically, Laguna bitumen showed a very significant drop in damage

Table 2 Damage parameters for the silicon crystal substrate (200 μm films)

Bitumen	Intact bitumen films				Notched bitumen films			
	S_A (10^{-2})	A_f	D_R (%)	Visual rating of stripping	S_A (10^{-2})	A_f	D_R (%)	Visual rating of stripping
L180 at 40 °C	nd	0.058	16	Small spot	0.03	0.083	23	Large spot
L180 at 50 °C	0.07	0.087	24	Large spot	0.18	0.200	55	Severe
L180 at 60 °C	0.19	0.221	61	Severe	0.26	0.254	70	Severe
L180 + Duomeen at 50 °C	nd	0.022	6	None	nd	0.040	11	None
L180 + Duomeen at 60 °C	nd	0.033	9	None	nd	0.047	13	Small spot
L180 + Redicote at 60 °C	nd	0.036	10	None	nd	0.054	15	None
A180 at 50 °C	nd	0.025	7	None	–	–	–	–
A180 at 60 °C	nd	0.036	10	Small spot	nd	0.040	11	Small spots
A180 + Duomeen at 60 °C	nd	0.018	5	None	nd	0.036	10	None
A180 + Redicote at 60 °C	nd	0.022	6	None	nd	0.040	11	None
M180 at 50 °C	nd	0.025	7	None	–	–	–	–
M180 at 60 °C	nd	0.033	9	Small spot	0.03	0.098	27	Large spot

nd = not determined because phase 2 was not exhibited during the test as observed from absorbance-time plots

A_w = 0.363 for silicon substrate

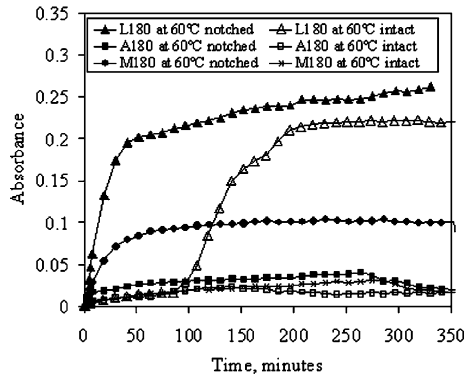

Fig. 4 Influence of film notching on the stripping process at 60 °C using three different bitumens of pen grade 180

parameters irrespective of the temperature and presence or absence of a notch in the film. However, there appears to be no significant difference between the D_R values of Duomeen and Redicote modified bitumen films. Figure 5 shows a very significant reduction in the damage of Laguna bitumen films at 60 °C. Even the notched films showed substantial reduction after modification with amine additives. It can be noticed from Fig. 5 that for modified Laguna bitumens, the shapes of absorbance curves support the assumption of diffusion. This is because there is no difference between notched and intact films, indicating that notching did not avail an alternative pathway for water. In other words, any water molecules that were detected by ATR moved across bitumen films and not via the notch. This observation also indicates that no water moved across the boundary between bitumen films and the brass frames.

Displacement of bitumen by water is considered to be influenced by consistency of the bitumen, which suggests that bitumen penetration perhaps plays a role in the resistance of bitumen to displacement by water. Four bitumens of different penetration grades (60/70, 70/100, 160/220 and 320/400) but from one and the same source (Laguna, Venezuela), were tested at 60 °C with water exposed intact films using the silicon crystal (cf. Fig. 6). As indicated, the final OH absorbance obtained with pen grade 60 bitumen was the lowest, followed by pen grade 85. Pen grades 180 and 370 did not show a significant difference in final absorbance. Randomness in the onset of the stripping phase is also noticed because L370 begun stripping earlier than L180.

Results obtained using zinc selenide crystal

Several tests were conducted using zinc selenide crystal for different plain and amine-modified bitumens. The results are listed in Table 3. As compared to the silicon crystal, zinc selenide seems not to show significant differences in damage parameters between the 180 pen grade bitumens used. However, there seems to be some reduction in the damage parameters for plain bitumens, when temperature was reduced from 60 to 50 °C. It therefore appears that the observed differences in moisture damage on the zinc selenide crystal may have more bearing on temperature than the type of bitumen used in making the thin films.

The results indicate that modification of bitumen with 0.5% Duomeen resulted in somewhat greater reduction in damage compared to 0.5% Redicote. This in turn may indicate that it makes a difference from the point of view of moisture damage which type of additive is added to bitumen before applying it to the substrate.

The influence of bitumen film thickness was examined by carrying out tests on a limited number of specimens using 180 pen grade bitumens at 60 °C. Film thicknesses of 200 and 400 μm were used on zinc selenide crystal, and the results are presented in Fig. 7. Essentially, very little water entered the interface of

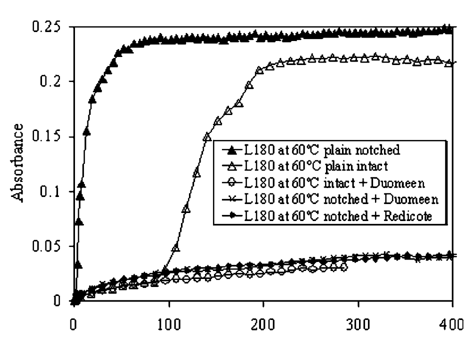

Fig. 5 Influence of amine additives on the stripping of Laguna bitumen at 60 °C using silicon substrate

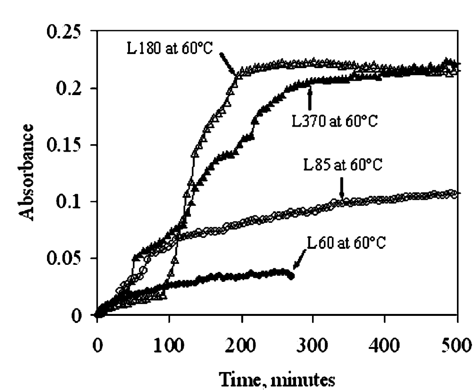

Fig. 6 IR absorbance data for intact bitumens of different pen grades, at 60 °C using silicon substrate

Table 3 Damage parameters for zinc selenide crystal substrate (200 μm intact films)

	Plain bitumen		+ 0.5% Duomeen		+ 0.5% Redicote	
	S_A (10^{-2})	D_R (%)	S_A (10^{-2})	D_R (%)	S_A (10^{-2})	D_R (%)
L180 at 50 °C	nd	5	nd	3	nd	3
L180 at 60 °C	0.06	15	nd	6	nd	10
A180 at 50 °C	nd	9	nd	3	nd	10
A180 at 60 °C	0.02	14	nd	4	nd	12
M180 at 50 °C	nd	8	nd	7	nd	9
M180 at 60 °C	0.04	15	nd	8	0.01	11

nd = not determined because phase 2 was not exhibited during the test as observed from the absorbance-time plots

bitumen and zinc selenide substrate for the 400 μm films, but a reasonable amount of it entered the interface for 200 μm films. Since water and bitumen are not compatible systems, it appears that as the bitumen film becomes thicker, the amount of water that can afford to pass through the bitumen to get into the interface becomes less.

Substrate dependence of water intake at the interface

Substrate surface chemistry seems to have an impact on rate and total uptake of water across bituminous films into the interface. As a consequence, the extent of displacement of bitumen films from their surfaces by water possibly varies. Results of some tests that were carried out on three crystal surfaces used are listed in Table 4. The results indicate that on the whole, bitumen films tested on silicon and germanium crystals exhibited more moisture damage than those tested on zinc selenide crystals. For silicon and germanium crystals, the highest loss of adhesion was exhibited by Laguna bitumen. This observation did not hold for the zinc selenide crystal. For example, Laguna and Arabian bitumens did not appear to differ (D_R values of 15 and 14, respectively), when tested on zinc selenide at 60 °C. However, for the germanium crystal, Laguna

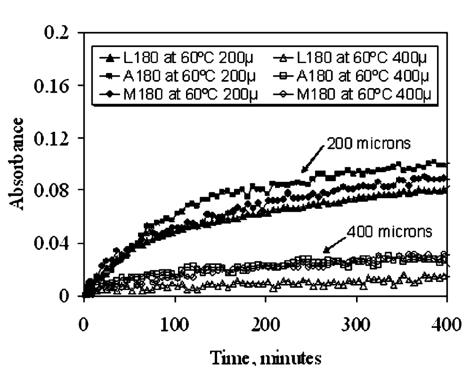

Fig. 7 Intensity changes for three bitumens of pen grade 180 at 60 °C using two different film thicknesses (zinc selenide substrate)

bitumen showed less damage at 50 °C than when tested on silicon crystal. In addition, after notching the film, Arabian bitumen tested at 60 °C showed higher damage with germanium crystal (D_R = 30) compared to silicon crystal (D_R = 11).

Silicon substrate contains a thin protective layer of silicon dioxide (SiO_2) as indicated in [8]. Similarly, germanium, placed immediately below silicon in the same group of the periodic table, possesses germanium dioxide (GeO_2) as a protective layer [9]. The surface chemistry of zinc selenide could not be established. As the exact chemistry of the zinc selenide surface was not known, it was not easy to explain why differences in results occurred on zinc selenide on one hand, and silicon and germanium on the other. Since this is an interesting problem area, more research involving determination of detailed surface chemistries of the substrates and the bitumens is needed.

Agreement between tests

In order to determine the agreement between different tests performed on similar materials using the method, several tests were conducted. This information is valuable in gauging the strength of this method in discriminating poor and good bitumens with regard to stripping. Tests were carried out by two persons using the same equipment under the same conditions within a reasonable time interval. The first series of tests (six replicates) were performed on Laguna pen grade 180 bitumen at 60 °C using notched films on silicon substrate. These tests were performed because they had shown stripping at this temperature. Other tests (five replicates) were performed using bitumens that did not exhibit stripping with silicon substrate. Three of these were notched Arabian pen grade 180 at 60 °C and two were notched Mexican pen grade 180 at 50 °C.

Results from the two series of tests above were compared. It was found out that tests on bitumens that did not exhibit stripping showed reasonable agreement. In contrast, the bitumens that were

Table 4 Some results of damage parameters for all the crystals used

	Si crystal		ZnSe crystal		Ge crystal	
	S_A (10^{-2})	D_R (%)	S_A (10^{-2})	D_R (%)	S_A (10^{-2})	D_R (%)
L180 at 50 °C	0.07	24	nd	5	nd	6
L180 at 60 °C	0.19	61	0.06	15	0.10	60
L180 + Duomeen at 50 °C	nd	6	nd	3	nd	10
L180 + Duomeen at 60 °C	nd	9	nd	6	nd	15
A180 at 60 °C	nd	10	0.02	14	nd	11
*A180 at 60 °C notched film	nd	11	–	–	nd	30

nd = not determined because phase 2 was not exhibited during the test as observed from the absorbance-time plots

* Only test with notched films, the rest of the tests were of intact films

stripped from the substrate showed poor agreement between tests as illustrated in Fig. 8. The 95% confidence interval for the mean curve of the non-stripping bitumens was constructed and its upper limit is included in Fig. 8. This interval was constructed by linearizing the data through fitting it on a theoretical power curve. The residuals of the linear fitted curve were found to be reasonably independent and normally distributed with zero mean and constant variance. With the assumptions of statistical analysis satisfied, the upper confidence limit (UCL) of this interval was regarded as the borderline between the stripping and the non-stripping bitumens with a 95% confidence. In other words, if the results of testing gave a curve above the UCL, the corresponding bitumen would be considered to have stripped. As shown in Fig. 8, the results of the bitumens that stripped are significantly above the UCL.

It was noted that the bitumens that stripped fell into two groups. One was of curves with a larger slope for the steepest part (four tests), and the other was of curves having a smaller slope (two tests). Visual observations of the bitumen films after the tests for these two groups, revealed differences in the way the bitumen deformed during stripping. Films of the first group deformed by moving towards both the long and short axes of the crystal. The second group showed preferential movement towards the long axis than the short axis. This observation seems to indicate that the displacement of bitumen during stripping exhibited two deformational fronts. The choice between the two fronts possibly depends on the geometry of the notch that is made in the film.

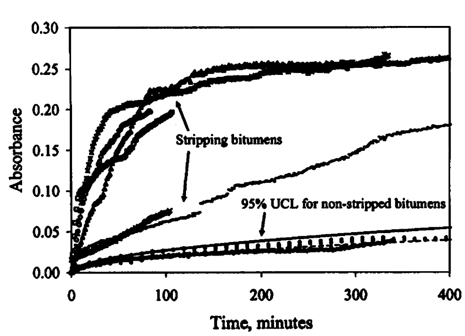

Fig. 8 Agreement in results of stripped and non-stripped samples using silicon substrate at 60 °C

Conclusions

Based on the results presented in this paper, the following conclusions can be drawn:

1. The proposed technique based on FTIR-ATR provided interesting information on transport of water into the bitumen/substrate interface, as well as characterization of stripping of bitumen from the substrates studied. Stripping bitumens were distinguished from bitumens that did not strip.
2. At least one of three processes occurred, namely random water diffusion, sudden film fracture and bitumen displacement by water at substrate surfaces. The process of water diffusion did not follow Fick's law.
3. Stripping as measured in this study was found to be influenced by bitumen source, when tested on silicon and germanium substrates. Testing using zinc selenide substrate did not show such a difference between the bitumens studied.
4. Initiating the stripping process by notching resulted in immediate commencement of water entry into the interface for the bitumens that showed stripping. No significant effect was observed for the non-stripping bitumens.
5. Addition of 0.5% amine additives significantly reduced stripping in the bitumen that was sensitive to damage even after notching. No significant differences in effectiveness were observed between the two additives on silicon and germanium substrate.

6. Silicon and germanium substrate crystals were more effective in distinguishing moisture damage between bitumens of diverse acidity compared to zinc selenide substrate.
7. There was reasonable agreement between tests on the bitumens that did not strip. The bitumens that stripped showed poor agreement between tests.

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