Durability of asphalt mixtures: Effect of aggregate type and adhesion promoters

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A B S T R A C T

Asphalt road–pavements are sensitive to water ingress, which degrades the bitumen to aggregate adhesion, promoting failure. The effects of water on a range of asphalt systems have been quantified using peel tests. The bitumen binder on an aluminium backing was peeled from the aggregate fixed arm and the fracture energy was determined. In dry conditions, failure was cohesive within the bitumen, but became mainly interfacial between the bitumen and aggregate after immersion in water. The effect of water on the adhesion of bitumen to three aggregates (limestone, marble and granite) was evaluated. Acidic aggregates (granite) showed a greater loss of adhesion than basic aggregates (limestone and marble) under wet conditions. The porosity of the aggregates, although shown to be significant, was less important than their chemical composition. The interfacial adhesion in wet conditions can be improved by mixing a silane, amine or rubbery polymer into the bitumen.

1. Introduction

Asphalt mixtures, consisting of mineral aggregates bound with a bitumen binder [1], are used extensively as road surface materials. Although asphalt is a relatively cheap material [1], the disruption to traffic flows and costs of replacing degraded road surfaces are significant, leading to a demand for more durable materials. Water is a major cause of such premature failure in asphalt. The resulting water damage causes a loss of stiffness and structural strength, due to the loss of adhesion between the aggregate and the bitumen, and/or loss of the cohesion within the bitumen binder [2–4]. Hence, an understanding of the adhesion mechanisms between the aggregate and bitumen is required if the durability performance of road surfaces are to be improved and an optimum selection of the asphalt component materials are to be made.

The effects of water on asphalt mixtures have been studied extensively. Both experimental and computational methods have been developed to assess their durability and their response to water ingress [4–12]. The experimental methods include qualitative tests conducted on loose bitumen-coated aggregate, such as the boiling test [7], and quantitative tests conducted on compacted asphalt mixtures [8], such as the Saturation Ageing Tensile Stiffness (SATS) test [10,11]. These approaches are frequently complex and not sufficiently sensitive to discriminate between the

performance of different types of bitumen binder and aggregates, and hence cannot give specific information on the nature of the bitumen–aggregate interface. Computational approaches have been developed to simulate the in-service conditions experienced by asphalt mixtures, and hence to predict their durability and water-resistance [5,6,13,14]. However, due to the lack of understanding of the adhesion mechanisms between the bitumen binder and the aggregates, and how such interactions are affected by the presence of water, these methods do not generally provide definitive guidance for selecting asphalt mixtures or for quantifying the improvement in performance from the addition of adhesion promoters.

Recently the present authors showed that a fracture mechanics approach can overcome these problems, and that such an approach can be used to quantify the effect of water damage in asphalt [15]. The use of the peel test [16–18] can avoid many of the problems associated with the viscoelastic nature of bitumen. The peel test allows the measurement of the adhesion between the bitumen and the aggregate (i.e. the adhesive fracture energy) and it has been adapted such that the water-resistance of different bitumen–aggregate combinations can be assessed following immersion in water for several days. By measurement of the fracture energy, the durability of bitumen–aggregate joints can be quantified [15]. This approach also provides information on the fracture path and evaluates the adhesive and/or cohesive strength of the joint.

Previous studies have indicated that the susceptibility of asphalt mixtures to attack by water is related to the mineralogy

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and surface texture of the aggregate, and also to the adhesion between the bitumen binder and the aggregates [1,4,19–21]. Airey and co-workers [4,12] assessed the water-damage of asphalt mixtures by comparing the stiffness of unconditioned and water-immersed specimens. It was found that significantly less water-damage occurred when basic aggregates, e.g. limestone, were used in the mixture than when acidic aggregates, e.g. granite [4] were used. In an attempt to explain this observation, both the physical and chemical properties of the aggregates were studied. Abo-Qudais and Al-Shweily [19] showed that a limestone aggregate had greater resistance to water-damage than basalt, and explained that limestone is positively charged, leading to stronger bonds, and as a result is a hydrophobic aggregate. They suggested that the chemistry of the aggregate affects the degree of water sensitivity of the bitumen–aggregate bond and noted that silica usually causes a reduction in bond strength between bitumen and aggregate; as the limestone aggregate contains less SiO_2 than basalt it shows a better resistance to water. Another study using granite aggregates also showed that the mineralogy of the aggregates has a significant impact on their adhesion to bitumen [20].

It is clear from the literature that the durability of asphalt mixtures (and hence the service life of road surfaces) depends, at least in part, on the adhesion between the bitumen and the mineral aggregates. In practice, the selection of the bitumen binder and aggregate during road construction is governed largely by economics: the cost of transporting the heavy aggregates any significant distance is prohibitive so the aggregates are sourced locally to the road construction site. Thus, the aggregates used on road surfaces reflect the local geology. For this reason there are wide variations in the durability of asphalt mixtures and various methods have been employed to improve them. For example, several methods have been used to reduce the extent of debonding (also known as stripping), including the addition of fillers, of polymers and of amine anti-stripping agents [22,23]. Also, organo-silanes have been successfully used to prevent stripping of asphalt mixtures [23–25].

In the present work a fracture mechanics approach has been followed to quantify the adhesion between the bitumen binder and the aggregate in selected asphalt mixtures. The fracture mechanics parameter, G_A, (or fracture energy) reflects both the energy required to break the intrinsic molecular forces associated with interfacial or cohesive failures and also the energy dissipated locally in the plastic or viscoelastic process zone at the crack tip. Attempts to improve the fracture energy therefore either work by increasing the intrinsic adhesion or by increasing the locally dissipated energy in the bitumen. The first objective of the work is to use the fracture mechanics approach to quantify the relationship between the water-damage performances of the asphalt mixtures as a function of the aggregates used. The second objective is to quantify the extent to which the water-damage performance can be improved by the use of various additives including silane and amine-based adhesion promoters and also the use of a polymer-modified bitumen.

2. Experimental

The peel test has been used in this work due to the viscoelastic and relatively low-modulus characteristics of the bitumen binder [15]. In this section, first the constituents of the asphalt mixtures are described and then the details of the adhesion promoters used are presented. Second, the experimental techniques employed including the peel test, the water exposure and the aggregate water uptake studies are presented.

2.1. Materials

The same grade of bitumen binder was used throughout this work and it was a medium penetration, 40/60 pen, provided by Shell Bitumen (Manchester). (The 'penetration' number is defined as the distance, expressed in tenths of a millimetre, travelled by a needle into the bitumen under a known load, at a known temperature for a known time [1].) Four different aggregates, each possessing a different chemical composition and porosity were studied, as shown in Fig. 1. Two basic aggregates, limestone and marble, and two acidic granite aggregates were chosen for study. Limestone has a relatively good resistance to water [1,4] and was therefore selected as the standard aggregate (for use in the control tests). Marble has a similar chemical composition to limestone but is less porous, and was selected so that the effect of aggregate porosity on the resistance to water could be studied. Limestone is a sedimentary rock and is composed of calcium carbonate fossils, while marble is recrystallised into interlocking calcite crystals [26]. The two granites were selected as they are reported to impart poor resistance to water to the asphalt mixture [20]. The chemical compositions of the aggregates, analysed using mineralogy analysis (MLA) by the University of Nottingham, are summarised in Table 1. (MLA uses backscattered electron (BSE) and energy dispersive X-ray (EDX) signals obtained using scanning electron microscopy to determine mineral composition. Comparison with a database of minerals and image processing allows particle boundaries and minerals to be identified.)

Three strategies to improve resistance to water, namely the use of silanes, amine anti-stripping agents and polymer modifiers were compared. The two silanes selected were supplied by Sigma Aldrich. The first was trimethoxy(octyl)silane (TMOS) which has a short carbon chain plus the silane functional group. The second silane was 3-(2-aminoethylamino) propyltrimethoxysilane (APT-MOS) which has two additional amino-functional groups. The silanes were mixed individually into the bitumen at a ratio of 0.5% v/v. In addition, a commercial amine-based anti-stripping agent (ABAA) was used, supplied by the University of Nottingham. Finally, a polymer modifier was used and this was a styrene-butadiene-styrene (SBS) copolymer, supplied also by the University of Nottingham. The anti-stripping agent and the polymer modifier were directly mixed into the heated bitumen prior to making the peel test specimens. The materials used are summarised in Table 1, where the silica and carbonate contents are given.

2.2. Peel test description and procedure

In the peel test, a flexible arm (the peel arm) is bonded to a rigid substrate (the fixed arm) with an adhesive [15,17]. The flexible arm is then peeled from the fixed arm and the peel force
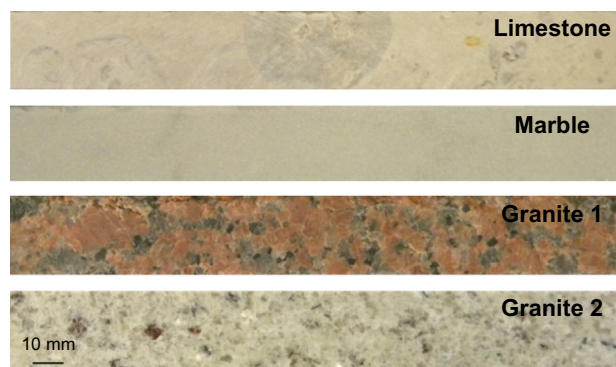
Fig. 1. Images of the four aggregates.

Table 1
List of materials used.

Material	Type	Chemistry	Comments, abbreviation
Bitumen	40/60 pen	—	Medium hardness
Aggregate	Limestone	> 98% calcite ($CaCO_3$)	Sedimentary, basic
	Marble	> 99% calcite ($CaCO_3$)	Metamorphosed limestone, basic
	Granite-1	38% quartz (SiO_2), 17% K-feldspar ($KAlSi_3O_8$)	Igneous, acidic
	Granite-2	25% quartz (SiO_2), 51% K-feldspar ($KAlSi_3O_8$)	Igneous, acidic
Adhesion promoter	Trimethoxy(octyl)silane	$CH_3(CH_2)_7Si(OCH_3)_3$	TMOS
	3-(2-Aminoethylamino) propyltrimethoxysilane	$NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3$	APTMOS
	Amine-based antistripping agent	Confidential	ABAA
	Polymer modifier	Styrene-butadiene-styrene	SBS

is measured. In this work, the fixed arms were made from the various aggregates and the bitumen acted as the adhesive. The flexible peel arm consisted of 0.2 mm thick aluminium (grade: EN AW-1200). This material provided good adhesion to the bitumen and therefore was selected as an effective 'carrier' for the bitumen. The rigid aggregate substrates were wet-sawn from boulders to a size of 200 mm long, 20 mm wide and 10 mm thick [15].

2.2.1. Sample preparation

The peel specimen used is shown schematically in Fig. 2. To manufacture each peel specimen, the aluminium peel-arm was grit-blasted on both sides using 180/220 mesh alumina grit. (Grit-blasting on both sides eliminated the residual stresses which arose from grit-blasting only one side [15], and which then led to debonding at the edges of the joints.) The peel arm was rinsed with running water to remove any grit, and cleaned with acetone to remove any grease or oil. The surface of the aggregate was wiped gently using a damp paper towel to remove any dust prior to bonding.

The bitumen was preheated for 30 min at 150 °C, to enable it to be readily poured. A 13 µm thick release-film of polytetrafluoroethylene (PTFE) was placed at one end of the bonding surface of the aggregate [15]. The heated liquid bitumen was then poured evenly onto the aggregate. The thickness of the bitumen layer, h_a, was controlled to be 0.25 mm using stainless steel wire spacers. The aluminium peel-arm was placed in an oven at 150 °C for 5 min and was then placed on top of the bitumen layer. Gentle pressure was applied using clamps to control the thickness of the bitumen layer, and the specimen was stored at ambient temperature (20 ± 3 °C) overnight. Finally, the excess bitumen on the edges of the specimen was removed using a knife-blade.

2.2.2. Water conditioning

Water was introduced into the peel joints after bonding by submerging the completed specimens in distilled water at 20 °C for up to 10 days. Hence, water permeated into the bitumen binder and the aggregate simultaneously, allowing it to directly attack the interface. (The aluminium peel arm is impermeable to water ingress.) The specimens were tested within a few hours of removing them from the water bath.

2.2.3. Test procedure

The peel tests were conducted at controlled ambient conditions of 20 ± 2 °C and 50 ± 5% relative humidity. The specimens were attached to a frictionless sliding trolley using two clamps (both outside of the length to be peeled). The flexible peel arm was gripped using the tensile grips of the test machine attached to the crosshead. The peel angle was set to 90° and a crosshead speed of 10 mm/min was used to ensure stable crack growth [15]. A minimum of three repeat specimens were tested for each condition. The peel force to initiate and propagate fracture was
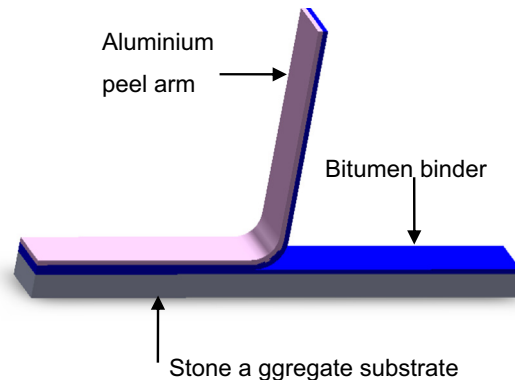

Fig. 2. Diagram of a 90° peel test.

recorded as a function of the displacement of the crosshead. After the initiation region, the steady-state crack propagation region was defined over an interval of 60 mm (between displacements of 20 mm and 80 mm), as shown in Fig. 3(a), and the mean force over this region was calculated. This steady-state propagation peel force, P, was used to determine the values of the adhesive fracture energy, G_A. To acquire further information on the peel fracture behaviour, photographs of the side of the specimen were taken during the test.

2.2.4. Data analysis

The adhesive fracture energy, G_A, was determined from the peel force using the approach outlined in the ESIS TC4 protocol for the determination of the adhesive fracture energy for flexible laminates using peel tests [16] and as described in detail for these joints in [15]. To summarize the procedure, the steady-state peel force was first used to determine the uncorrected adhesive fracture energy, G [16,17] using:

$$G = \frac{P}{b}(1 - \cos\theta) \tag{1}$$

where P is the steady-state peel force, b is the width of the specimen and θ is the applied peel angle, where $\theta = 90°$ in the present work. The corrected adhesive fracture energy, G_A, is then obtained using:

$$G_A = G - G_p \tag{2}$$

where G_p is the energy associated with the plastic bending of the peel arm. To determine G_p, a tensile test was performed on the peel arm material at the same test rate as the peel test. The test is described in [15], and a power-law fit to the post-yield stress/strain curve was used to define the parameters required for the energy correction. The value of G_p was then calculated using large displacement beam theory with modifications for plastic bending [16,17]. The software ICPeel was used for this analysis [18]. The
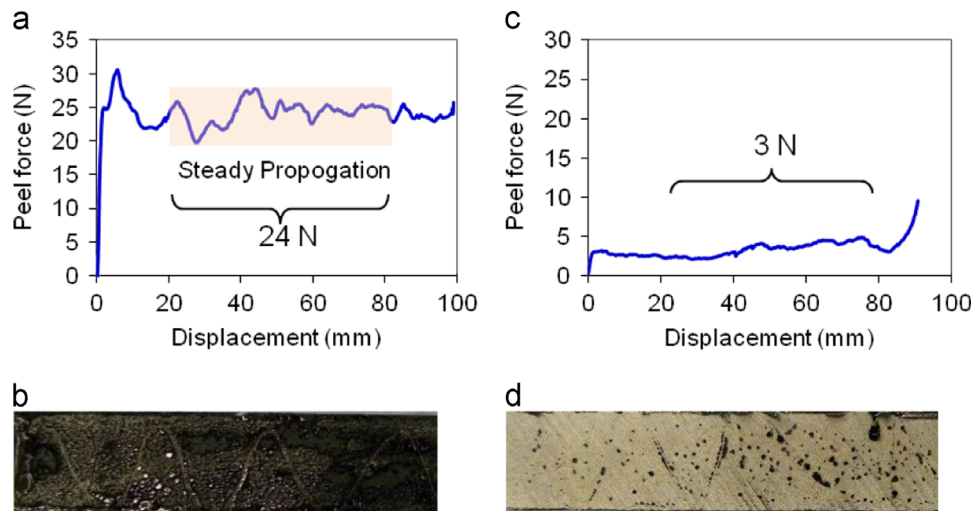
Fig. 3. Peel curves and images of the aggregate fracture surfaces for bitumen–limestone joints: ((a), (b)) dry specimen; ((c), (d)) water immersed for 10 days.

adoption of this approach for the bitumen–aggregate joint was discussed in detail in [15].

2.3. Water uptake tests

Water uptake tests were conducted to study the response of the different aggregates to water ingress. Specimens of each aggregate were sawn to dimensions of $20 \times 10 \times 4$ mm^3. They were dried at 60 °C for 24 h, and were then immersed in distilled water at 20 °C for up to 14 days to ensure that saturation was reached. The samples were removed at intervals, carefully wiped dry and were weighed on a balance to a precision of 1×10^{-5} g.

The rate of water ingress into aggregate and concrete is normally characterised by the sorptivity, which is the rate of water absorption due to capillary action. This may be measured by absorption against gravity, e.g. due to rising groundwater, by standing one end of a piece of aggregate in water and measuring the mass over time [27,28]. Alternatively, water uptake may be aided by gravity, e.g. when water ponds on a road surface, by making a dam around the sides of a piece of aggregate, filling this with water, and measuring the mass uptake by the aggregate over time [28]. In the present work, the peel samples will be immersed in water so it is most relevant to measure the absorption of the aggregate when immersed in water, e.g. [29,30]. The absorption, I, is given by [31]:

$$I = \frac{m_t}{A\rho} \tag{3}$$

where m_t is the change in specimen mass at time t, A is the exposed area of the specimen, and ρ is the density of water. The sorptivity is determined by plotting the absorption, I, against the square root of time. A linear regression was used to fit the initial linear portion of the uptake, and the sorptivity was calculated from the gradient.

3. Results and discussion

The four different aggregates studied gave a range of different durability performances as will now be presented and discussed.

3.1. Influence of aggregate nature and properties

3.1.1. The test method

Fig. 3(a) shows the peel force for a limestone aggregate control specimen (no water conditioning) as a function of the crosshead displacement. After the initiation of peeling, an approximately steady-state peel force was achieved. For the three repeat specimens, a mean steady-state peel force of 23 N was measured, and the typical variation was ± 2 N. The average fracture energy, G_{A0}, of the dry specimens was calculated to be 619 J/m^2. A standard deviation of ± 32 J/m^2 (i.e. $\pm 5\%$) between specimens was calculated, which was considered reasonable as both aggregate and bitumen are natural materials, and hence a relatively high degree of variability is expected. Failure was cohesive within the bitumen, i.e. leaving a layer of bitumen covering the aggregate, see Fig. 3(b). The peel specimens using the limestone aggregate were immersed in water for periods of up to 10 days. Table 2 shows that the adhesive fracture energy, G_A, decreases with increasing conditioning time, indicating how fast and how significant the effect of water was on the performance of the bitumen–aggregate joint. After 1 day of immersion, the fracture energy has decreased to 34% of the dry value, and after 10 days, the fracture energy had fallen to 12%. Here the peel force had reduced to only a few Newtons, see Fig. 3(c).

The dimensionless ratio of the two fracture energies, G_A/G_{A0}, is used to represent the water sensitivity of the joints. The value of G_A/G_{A0} decreased continuously with increasing conditioning time. As shown in Fig. 3(d), there was very little bitumen residue remaining on the aggregate surface of the wet specimens, indicating interfacial failure occurred between the limestone aggregate and the bitumen in the water-immersed specimens. The test method has thus effectively identified the effects of water even after these short immersion times. Based on our previous research, water-induced damage is mainly attributed to a reduction in the interfacial adhesion between the bitumen and the limestone aggregate. The cohesive strength of the bitumen binder remains relatively unaffected by the presence of ingressing water [15].

3.1.2. The peel tests

When tested in the dry condition (no water exposure), cohesive failure was observed for all four aggregates, indicating good interfacial adhesion between the bitumen binder and all the aggregates. The measured fracture energies are shown in Table 3, and these lie in the range of 540 J/m^2 to 710 J/m^2. The

Table 2
Fracture energies from dry and water-immersed peel joints made using 40/60 pen bitumen binder with the limestone aggregate.

Conditioning	Time	P	G_A (J/m^2)		G_A/G_{A0}	Observed locus of failure
	(days)	(N)	Mean	SD		
Dry	0	23	619	32	1.00	Cohesive
Wet	1	10	212	135	0.34	Mainly interfacial, some cohesive
	3	12	281	32	0.45	Mainly interfacial
	5	7	137	32	0.22	Interfacial
	7	8	167	100	0.27	Interfacial
	10	4	77	18	0.12	Interfacial

Table 3
Fracture energies from dry and water-immersed peel joints made using 40/60 pen bitumen binder with the different aggregates.

Aggregate and conditioning		Time	P	G_A (J/m^2)		G_A/G_{A0}	Observed locus of failure
		(days)	(N)	Mean	SD		
Limestone	Dry	0	23	619	32	1.00	Cohesive
	Wet	3	12	281	32	0.45	Mainly interfacial
		7	8	167	100	0.27	Interfacial
Marble	Dry	0	20	541	18	1.00	Cohesive
	Wet	3	21	573	32	1.06	Mainly cohesive
		7	20	517	94	0.96	Mainly cohesive
Granite-1	Dry	0	25	706	45	1.00	Cohesive
	Wet	3	9	183	63	0.26	Interfacial
		7	5	79	24	0.11	Interfacial
Granite-2	Dry	0	23	637	20	1.00	Cohesive
	Wet	3	1	22	8	0.03	Interfacial
		7	2	34	21	0.05	Interfacial

measured fracture energy represents the cohesive value for the 40/60 pen bitumen binder, and the variations may be attributed to experimental scatter.

When the bitumen–aggregate joints were immersed in water, with the exception of marble, the fracture energies reduced. The results are shown in Table 3 for immersion times of 0, 3 and 7 days. The aged values measured using the basic aggregates (i.e. marble and limestone) were much higher than for the acidic aggregates (i.e. granite-1 and -2). The steady-state peel forces and the fracture surface appearances for the '3 days' immersed specimens are also shown in Fig. 4.

3.1.3. Water uptake in the aggregates

Before the results for the water-immersed peel joints are discussed in detail, it is useful to consider the water uptake results, as shown in Table 4. The limestone aggregate was found to absorb approximately seven times as much water as the marble. The sorptivity values show that limestone absorbs water much more quickly than marble. This is expected as marble is formed by metamorphism (re-crystallisation) of limestone, and is therefore much less porous than limestone [26]. Granite-2 was shown to absorb water most quickly, with a sorptivity of about twenty times that of the marble. As can be seen in Table 4, the equilibrium water uptake value of granite-1 was approximately the same as for granite-2, but the rate of uptake was slower. Thus, granite-2 will saturate very quickly, as uptake is fast and the equilibrium uptake is low.

3.1.4. Interpretation of the wet peel tests

Good performance after water immersion was expected for the bitumen–limestone joints, and although the fracture energy decreased with immersion time, this system retained 27% of the dry fracture energy after 7 days. This performance was superior to both systems comprising granite aggregates, as will be discussed below. The two basic aggregates, limestone and marble, both comprise $> 95\%$ $CaCO_3$, so marble would be expected to show good resistance to water. This was observed, as the fracture energy measured for the marble joints was unaffected by water immersion. It can be seen in Fig. 1 that the marble has finer mineral grains and is denser than limestone, this greatly reduces the rate of water uptake and the saturation value, as was shown in Fig. 5, compared to the more porous limestone. The limestone absorbs approximately 7 times as much water as marble, as shown in Table 4, and the sorptivity was measured to be approximately 15 times that of the marble. The time taken for the limestone aggregates to saturate can be calculated to be less than 6 h assuming that the uptake of water is linear following the sorptivity. If the full absorption behaviour is considered, then saturation occurs within 30 h. Thus the porous nature of the limestone transports water rapidly to the interface where it can attack the aggregate–bitumen interface relatively quickly, leading to more interfacial failure and a lower fracture energy, as shown in Table 3. In contrast, the less porous marble aggregate transports much less water to the bitumen–aggregate interface and as a consequence this system shows mainly cohesive failure. These results demonstrate that the durability of the various test specimens can at least in part be explained by the differing density and porosity of the aggregates, quite apart from their chemistry. It is also noteworthy that the more porous aggregates have been reported to absorb more bitumen at the surface, leading to a stronger bond between the bitumen and aggregates under dry conditions [19]. However, although the fracture energy for the more porous limestone joint was higher than that of the marble joint under dry conditions, the difference was not statistically significant.

For the bitumen-granite aggregate joints, interfacial failure and a significant reduction in the fracture energy were observed after conditioning in water for 3 days. The poor water performance observed was expected because granite is an acidic aggregate and has been previously reported to show poor water-resistance [4]. The chemical structure of granite is much more complex than that of limestone or marble. Granite is formed of individual grains of many different minerals, including quartz, albite and feldspar as the major constituents of granite-1. The nature, size and the distribution of these various grains can significantly affect the adhesion between the granite and bitumen. For example, feldspar has been found to give poorer adhesion than the other types of grains [20]. The water uptake results in Fig. 5 demonstrate that the two granites absorbed very similar amounts of water at saturation (granite-1 absorbs 0.41%, and granite-2 absorbs 0.49%). Although these uptake values are less than for limestone, the G_A/G_{A0} value of the granite-2 joints was only 3% after 3 days of conditioning, whereas G_A/G_{A0} for the granite-1 joints was 26%. These fracture energy values show that granite-2 has very poor water-resistance, even compared to granite-1. However, granite-2 also had a much higher sorptivity than granite-1, so that would at least partly explain the more rapid loss of fracture energy in the granite-2 joints. Assuming linear uptake, a granite-2 joint will saturate fully within 2 h. For the full absorption behaviour, saturation occurs within 10 h. A K-feldspar content of 51% and a quartz content of 25% (see Table 1) make granite-2 relatively hydrophilic. The physical and chemical characteristics of the aggregates both clearly influence the durability performance of the joints, but the a comparison of the fracture energy results between limestone and granite-2 joints (where the sorptivity values are similar but
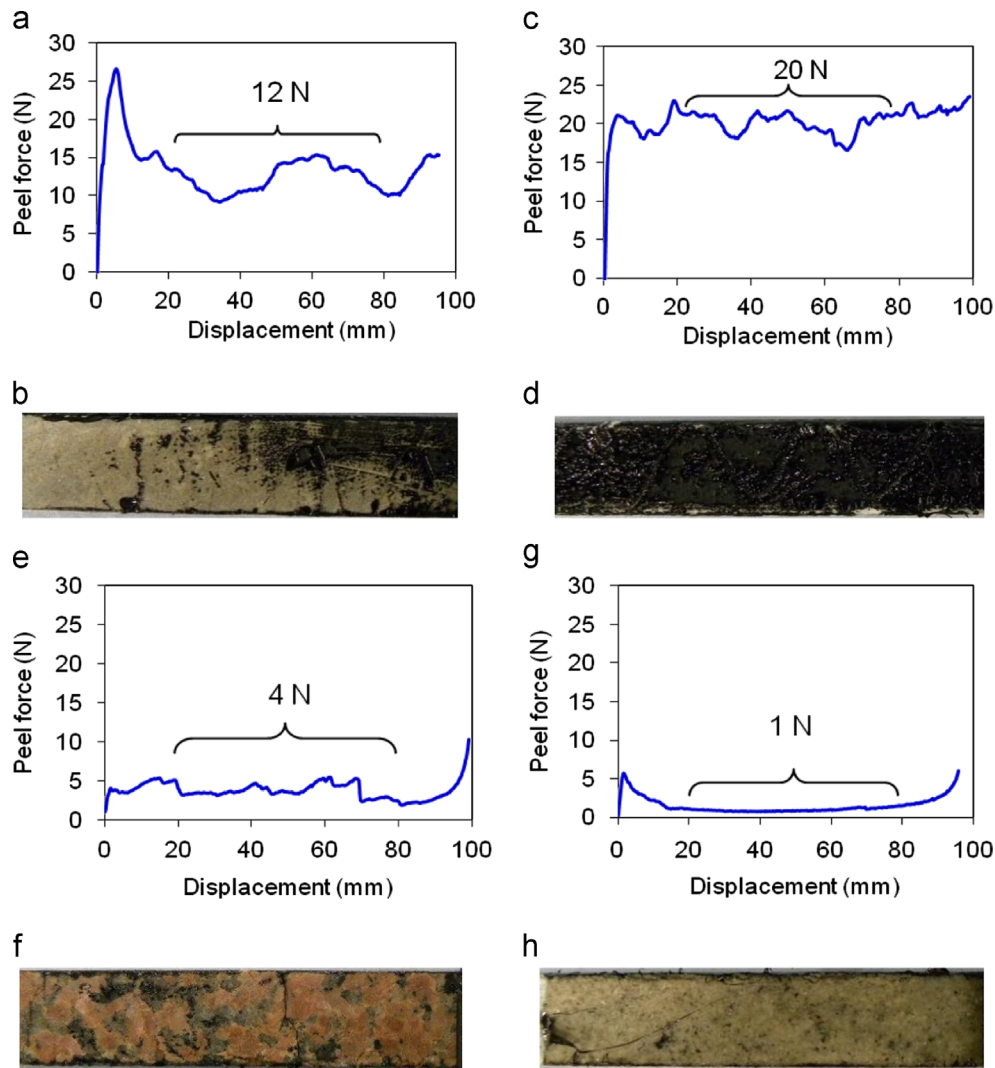
Fig. 4. Peel curves and images of the aggregate fracture surfaces after water conditioning for 3 days, using: ((a), (b)) limestone; ((c), (d)) marble; ((e), (f)) granite-1; ((g), (h)) granite-2 aggregates.

limestone absorbs water to a higher concentration and has the superior water performance) would suggest that the chemical structure of the aggregates is a more important factor than the amount of water uptake at saturation. Therefore, techniques which can exploit these various chemical structures and target weakly performing mineral grains may be particularly beneficial. Some techniques are examined in the following section.

3.2. Effect of modifiers

3.2.1. Introduction

The results have shown that the aggregate used greatly affects the water-resistance of the aggregate–bitumen joints. To investigate how this resistance could be improved, three types of modifiers were studied: two silanes, one amine anti-stripping agent, and one polymer modifier. Three aggregates were used, namely: limestone, marble and granite (granite-2 was chosen as this showed the faster water uptake and the poorer performance in the peel tests after water immersion).

3.2.2. Silanes

Silane coupling agents have been successfully shown to promote adhesion between organic and inorganic materials, e.g. polymers and

Table 4
Water uptake data for the four aggregates.

Aggregate	Sorptivity ($\times 10^{-3}$ mm/min$^{0.5}$)	Equilibrium water uptake (%)
Limestone	12.56	1.63 ± 0.04
Marble	0.84	0.24 ± 0.02
Granite-1	4.65	0.41 ± 0.03
Granite-2	17.93	0.49 ± 0.02

glass fibres [32], and to increase durability in wet environments [32]. Hence these were an obvious choice for investigation in the present study, to promote bonding between the organic bitumen and the inorganic aggregates. The two silanes used were trimethoxy(octyl) silane (TMOS) and 3-(2-aminoethylamino) propyltrimethoxysilane (APTMOS). TMOS contains a short C_8 carbon chain and a silane functional group -$Si(OCH_3)_3$. APTMOS has two amine groups in addition to the silane functional group. The silanes were mixed into the hot bitumen at 0.5% by volume prior to forming the bitumen–aggregate joints.

When the joints were tested dry, all failure was cohesive and the fracture energies were very similar to those for the dry control specimens, see Table 5. Hence, as expected, the addition of the
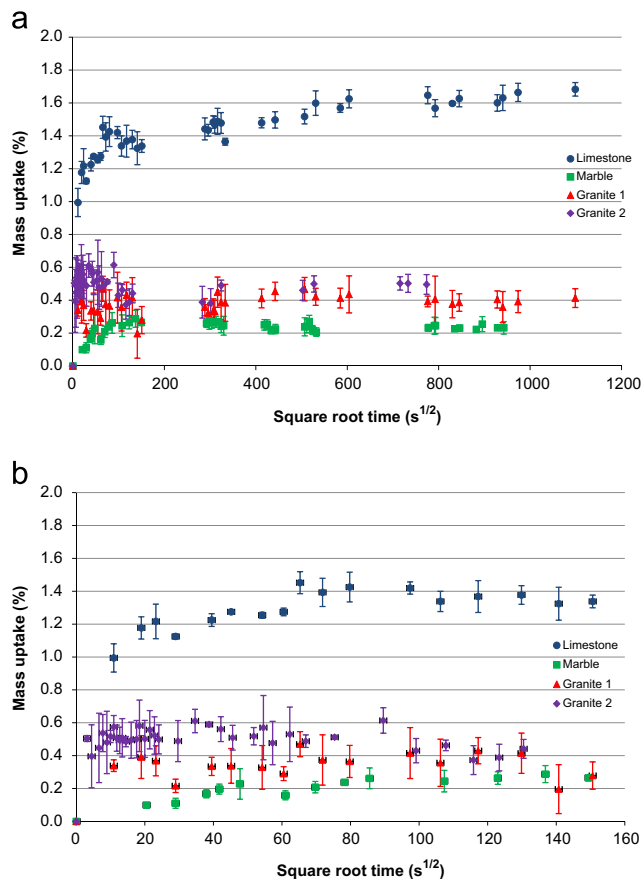
a

b

Fig. 5. Percentage water uptake versus time for limestone, marble, granite-1 and granite-2, (a) uptake to saturation; (b) uptake at short times.

Table 5
Fracture energies for dry and 3-day water-immersed peel joints using unmodified, silane-modified, and amine-based antistripping agent-modified bitumen with various aggregates.

Aggregate	Treatment and conditioning		P (N)	G_A (J/m²) Mean	SD	G_A/G_{A0}	Observed locus of failure
Limestone	Unmodified	Dry	23	619	32	1.00	Cohesive
	Unmodified	Wet	12	281	32	0.45	Mainly interfacial
	TMOS	Dry	20	517	34	1.00	Cohesive
	TMOS	Wet	17	423	54	0.82	Mainly cohesive
	APTMOS	Dry	22	601	34	1.00	Cohesive
	APTMOS	Wet	18	453	54	0.75	Mainly cohesive
	ABAA	Dry	23	626	29	1.00	Cohesive
	ABAA	Wet	19	493	44	0.79	Mainly cohesive
Marble	Unmodified	Dry	20	541	18	1.00	Cohesive
	Unmodified	Wet	21	573	32	1.06	Cohesive
	TMOS	Dry	20	538	18	1.00	Cohesive
	TMOS	Wet	18	459	65	0.85	Cohesive
	APTMOS	Dry	21	559	14	1.00	Cohesive
	APTMOS	Wet	16	406	85	0.73	Mainly cohesive
	ABAA	Dry	24	655	32	1.00	Cohesive
	ABAA	Wet	18	459	40	0.70	Cohesive
Granite-2	Unmodified	Dry	23	637	20	1.00	Cohesive
	Unmodified	Wet	1	22	8	0.03	Interfacial
	TMOS	Dry	20	527	20	1.00	Cohesive
	TMOS	Wet	20	538	61	1.02	Cohesive
	APTMOS	Dry	20	531	29	1.00	Cohesive
	APTMOS	Wet	14	318	37	0.60	Cohesive/interfacial
	ABAA	Dry	23	626	0	1.00	Cohesive
	ABAA	Wet	20	534	118	0.85	Cohesive/interfacial

silane does not affect the performance of the bitumen in dry conditions. After 3 days of water conditioning, the results in Fig. 6 and Table 5 show that using TMOS gave an improvement in fracture energy, as can be observed for all three types of modified bitumen–aggregate joints compared to the unmodified bitumen. Mainly cohesive failure occurred in the joints made using all three aggregates with the TMOS-modified bitumen, as shown in Fig. 6. It is clear that the silane is able to diffuse through the bitumen to reach the surface of the aggregate and enhance the adhesion. The most significant enhancement in the fracture energy was shown to occur between the bitumen–aggregate joints with granite-2. Here cohesive failure was observed for the TMOS-modified bitumen after 3 days of water conditioning, with $G_A/G_{A0}=1$, compared with interfacial failure and $G_A/G_{A0}=0.03$ for the unmodified bitumen. Silane coupling agents contain chemical functional groups that can react with silanol groups on the silica and therefore form strong covalent bonds. The other end of the molecule can interact, via inter-diffusion, with the bitumen, so forming a strong coupling between the aggregate and the bitumen. Bitumen consists of condensed hydrocarbon rings and is a highly hydrophobic material. On the other hand, the aggregates are highly hydrophilic, especially the silica containing granites. The presence of the silane at the interface will also make the surface less hydrophilic, leading to the enhancement of the water-resistance [23].

The effect of the addition of APTMOS to the bitumen is shown in Fig. 7 and Table 5. An increase of fracture energy is seen in the joints made using both limestone and granite-2 compared to the unmodified bitumen. The failure is more cohesive than for the unmodified bitumen, see Fig. 7, but areas of interfacial failure are present. The enhancement was not significant in the joint made using marble, and may indeed even reduce the water-

resistance, since marble forms a durable bond to bitumen without silane treatment when water-immersed. In terms of performance enhancement, APTMOS was no more advantageous than TMOS, even though APTMOS contains additional amino-functional groups. For APTMOS, in addition to the covalent bond formed between –Si(OCH$_3$)$_3$ and the aggregates, the amino-functional groups can also form chemical bonds with the aggregates. Thus, the carbon chains may tend to lie along the surface rather than interacting with the bitumen as in the case of the TMOS, and therefore APTMOS is less effective than TMOS at improving the water resistance.

3.2.3. Amine-based anti-stripping agent

Amine-based anti-stripping agents which comprise of a long hydrocarbon chain and amine functional groups have been shown to be beneficial to bitumen–aggregate systems. The amine group reacts with the aggregate surface, while the hydrophobic hydrocarbon chain interacts with the binder, again via inter-diffusion. Hence, a bridge is formed between the hydrophilic aggregate and hydrophobic bitumen, producing a relatively strong bond between them [33,34].

In this work, a commercial amine-based anti-stripping agent (ABAA) was used to modify the bitumen. The results in Fig. 8 and Table 5 show that the interfacial adhesion between the bitumen and both limestone and granite-2 aggregates has been improved by the addition of the ABAA to the bitumen after 3 days of immersion in water. Despite some interfacial failure in the joint prepared using granite-2, the fracture energy significantly increased from 22 J/m² to 534 J/m², indicating a significant improvement in the water-resistance of the joint following the amine treatment. For marble and limestone, relatively high fracture energies were also measured.

The addition of ABAA can increase the wettability of bitumen on the aggregates as the amine changes their surface properties [33]. Such an alkaline amine contains both amine-functional
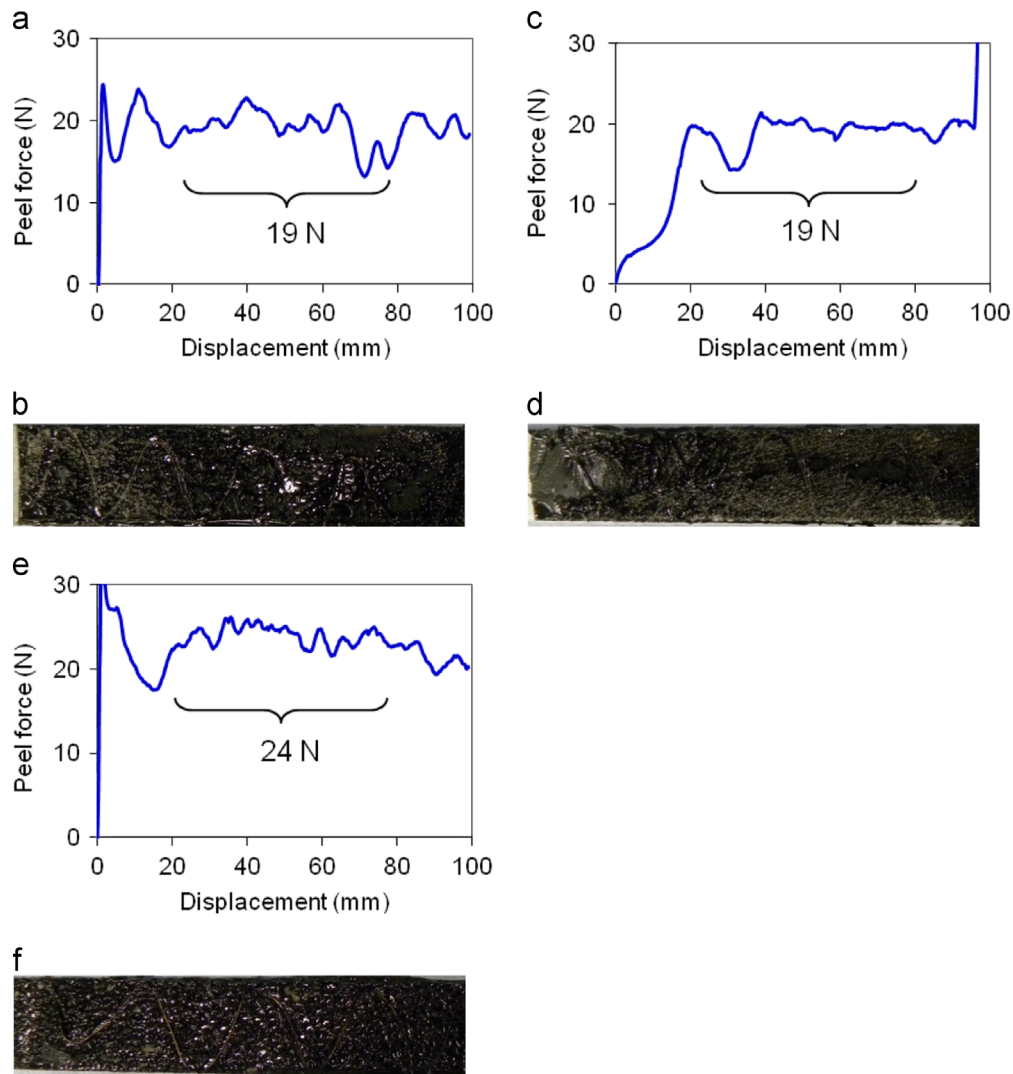
Fig. 6. Peel curves and images of the aggregate fracture surfaces using TMOS-modified bitumen binder after water conditioning for 3 days, using: ((a), (b)) limestone; ((c), (d)) marble; ((e), (f)) granite-2 aggregates.

groups and a hydrocarbon chain. The hydrophobic hydrocarbon group is directed into the hydrophobic bitumen, forming a strong interaction. The amine group, on the other hand, reacts with the aggregate surface, forming a chemical bond. As a result, the amine antistripping agent acts as a bridge between the bitumen and the aggregates, providing a strong bond between them. This demonstrates that the amine-based anti-stripping agent is an effective method for improving the water-resistance of the bitumen–asphalt joints and may prove equally effective when added to asphalt road–pavement mixtures.

3.2.4. Styrene–butadiene–styrene

Polymer-modified bitumen is widely used to improve the durability of asphalt mixtures [22,35]. The polymer modifier used in this study was a styrene-butadiene-styrene (SBS) block copolymer. This is a thermoplastic elastomer, which can increase the elasticity of bitumen [22]. The polystyrene blocks form particles, which act like crosslinks and tie the polybutadiene chains together to form a three-dimensional network. The polystyrene blocks reinforce the bitumen binder, while the polybutadiene imparts the elastomeric behaviour [22].

The SBS-modified bitumen binder was tested using only the limestone aggregate. In dry conditions a fracture energy of

1330 J/m^2 was measured, as shown in Table 6, and failure was cohesive within the bitumen, see Fig. 9(b). This is a dramatic increase in the fracture energy compared to the 619 J/m^2 for the unmodified 40/60 pen binder. During the peel test, there was a very large amount of bridging behind the peel front with the SBS-modified bitumen, as shown in Fig. 10(a). This demonstrates that the addition of SBS makes the binder relatively very ductile, which is due to the increase of viscoelasticity of the binder. In contrast, the standard 40/60 pen bitumen shows no, or only a small amount of bridging, see Fig. 10(b). As has been discussed in a previous study [22], the high strength and elasticity of the modified-bitumen are derived from the three-dimensional network formed by the physical crosslinking of SBS. The polystyrene end blocks provide the strength to the binder while the polybutadiene blocks make the material very elastic.

An enhancement due to the addition of SBS, compared to the unmodified binder, was also observed after water-conditioning for 3 days, where the fracture energy increased from 281 J/m^2 to 1120 J/m^2. Here the SBS-modified binder showed cohesive failure, see Fig. 9(d), whereas the unmodified binder showed mostly interfacial failure. Therefore, The SBS polymer modifier increased the viscoelastic properties of the bitumen, resulting in the remarkable increase of the fracture energies in both dry and wet conditions. It has been shown [22,35] that the SBS-modified
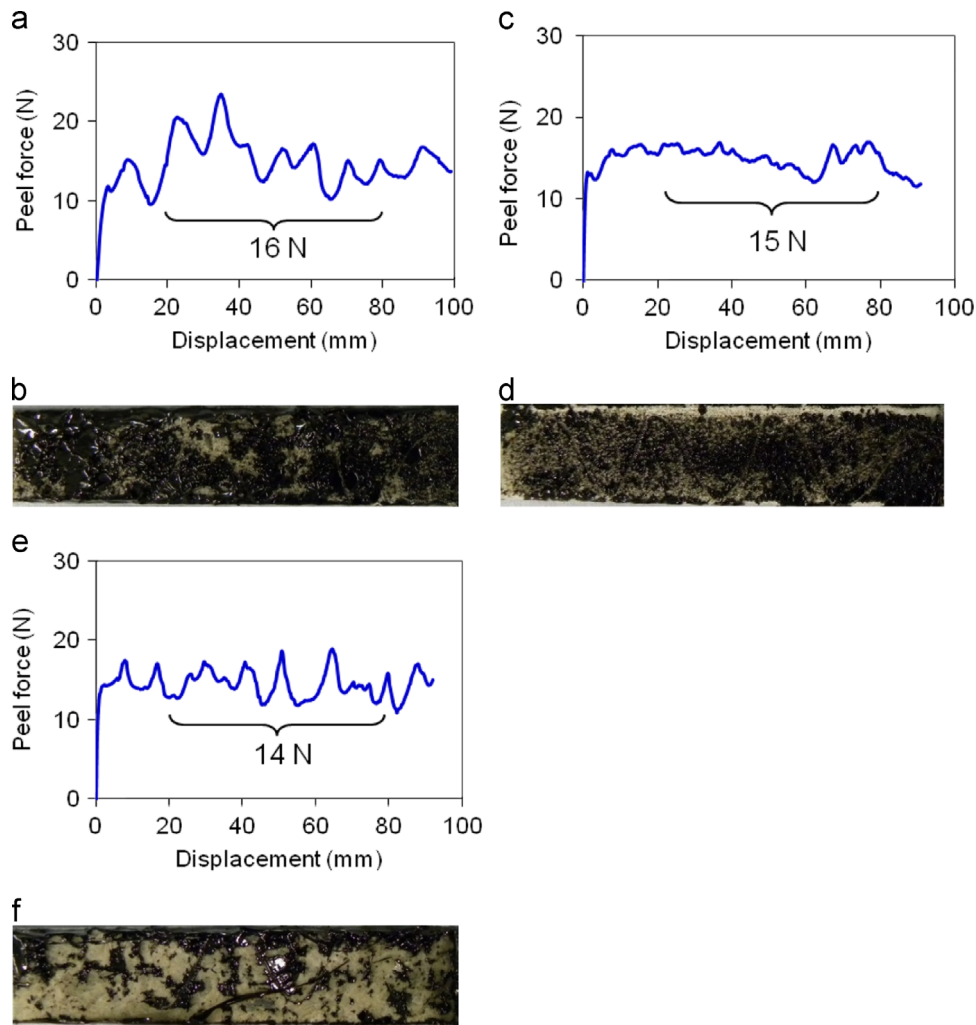
Fig. 7. Peel curves and images of the aggregate fracture surfaces using APTMOS-modified bitumen binder after water conditioning for 3 days, using: ((a), (b)) limestone; ((c), (d)) marble; ((e), (f)) granite-2 aggregates.

bitumen shows improved water-resistance by both producing a network within the binder and by increasing the adhesion between the binder and the aggregate. The present results clearly confirm that the addition of SBS is a useful method to enhance the durability of bitumen–asphalt joints and may prove extremely effective in asphalt road–pavement mixtures.

3.2.5. Comparison of modifiers

When tested in the dry condition using the peel test, three of the four modifiers did not increase the fracture energy of the bitumen–aggregate joints compared to the unmodified binder. This shows that the properties of the bitumen are unaffected by these modifiers. However, the addition of the styrene-butadiene-styrene copolymer gave a large increase in the fracture energy in the dry condition, due to an increase in the viscoelasticity of the binder. The locus of failure of the bitumen–aggregate joints was always cohesive in the binder in the dry condition.

When tested in the wet condition, the modification with SBS also gave good durability, an average value of $G_A/G_{A0}=0.84$ being measured after 3 days of water immersion. The locus of failure was also more cohesive than for the unmodified binder. When modified with the amine anti-stripping agent, the ABAA modified bitumen with gave a consistent performance after water conditioning, as the values of G_A/G_{A0} lie in the range of 0.70 to 0.85 for all of the three aggregates. When modified with the silanes, the

highest values of G_A/G_{A0} were measured using the TMOS-modified binder. However, too much emphasis should not be placed on the results with the marble aggregate as this is not a typical road construction material, even though the unmodified binder showed a high fracture energy and cohesive failure after conditioning for 7 days, with a G_A/G_{A0} value of 0.96. In general, the TMOS-modified bitumen showed the best water resistance, followed by the ABAA and the APTMOS modified-bitumens.

4. Conclusions

The water resistance of asphalt mixtures as widely used in the construction of road surfaces has been investigated in an experimental study. A peel test has been used to measure the adhesive fracture energy between a medium penetration grade bitumen (on a flexible aluminium backing) and four different aggregates: limestone, marble, and two types of granite. Limestone and marble were selected as examples of basic aggregate, and the two granites as examples of acidic aggregate.

The adhesive fracture energy was obtained from the steady-state peel force with suitable corrections for plastic deformation of the peel arm in tension and bending. Joints consisting of an aggregate fixed arm bonded to the flexible arm with the bitumen were immersed in water immersion for up to ten days. The peel tests were performed soon after removal from the water bath and
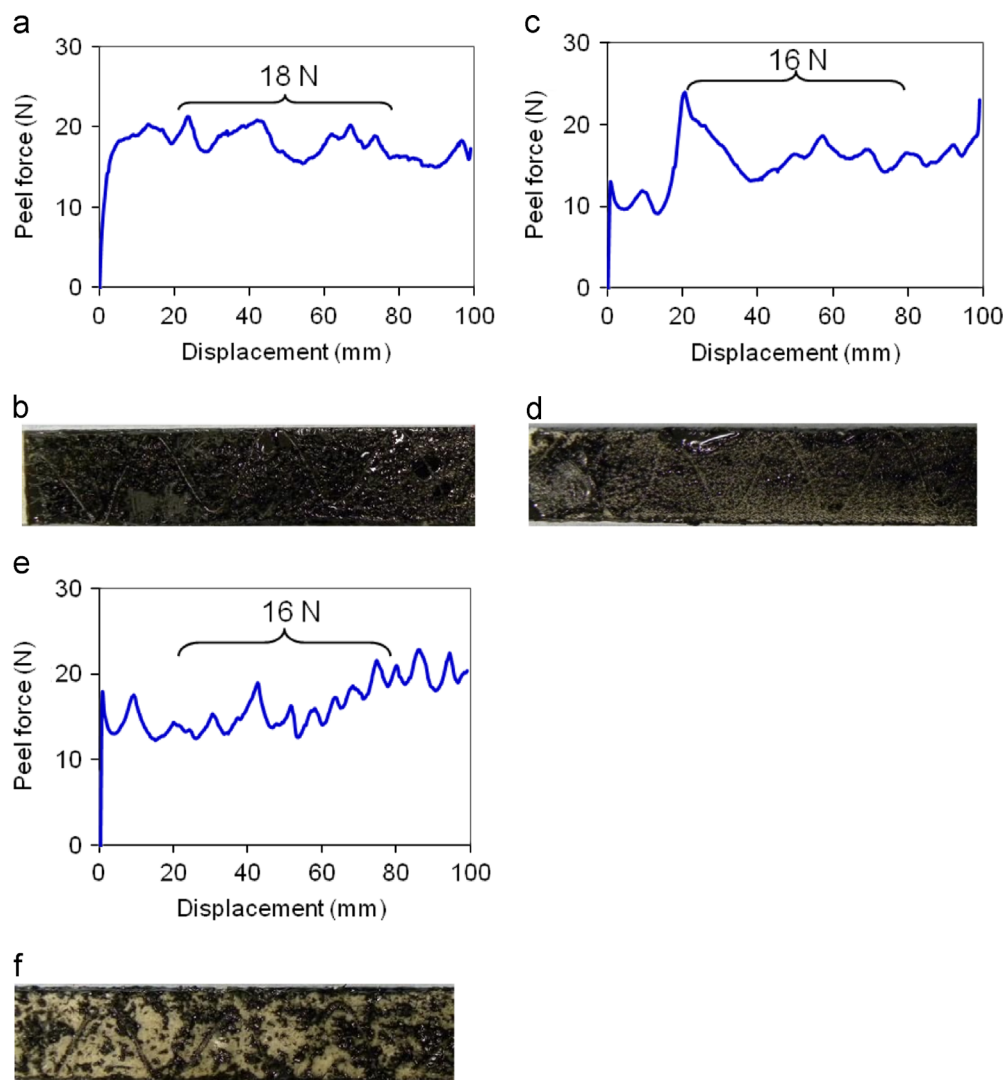
Fig. 8. Peel curves and images of the aggregate fracture surfaces using ABAA-modified bitumen binder after water conditioning for 3 days, using: ((a), (b)) limestone; ((c), (d)) marble; ((e), (f)) granite-2 aggregates.

Table 6
Fracture energies for dry and 3-day water-immersed peel joints made using SBS-modified bitumen binder with limestone aggregate.

Treatment and conditioning		P	G_A (J/m^2)		G_A/G_{A0}	Observed locus of failure
		(N)	Mean	SD		
Unmodified	Dry	23	619	32	1.00	Cohesive
	Wet	12	281	32	0.45	Mainly interfacial
SBS	Dry	41	1330	83	1.00	Cohesive
	Wet	36	1120	34	0.84	Cohesive

the fracture energy and locus of failure were determined. The rate of water absorption and the equilibrium water concentration were also measured for the aggregates. The results showed that the basic aggregates (limestone and marble) possessed a superior water resistance than the acidic aggregates (two types of granite). Within the basic group, marble is chemically similar to limestone, but shows a better water-resistance due its lower porosity. However, two aggregates with similar sorptivity values (limestone and the second granite) exhibited very different water sensitivities in the peel test, confirming that the aggregate chemistry was more important than porosity, as reported in the literature.

Adhesion promoters were successfully added to the bitumen to enhance the water resistance of the various bitumen–aggregate joints. The use of two different silanes and an amine anti-stripping agent were applied to all three joint systems (limestone, marble and the second granite). In addition, a styrene-butadiene-styrene (SBS) block copolymer modifier was investigated using joints containing the limestone aggregate. All were effective to a greater or lesser extent, but for silane modification the most significant improvement was found in the bitumen–granite joints. It was concluded that the addition of silane is a useful method to bridge the interface between the organic bitumen binder and the inorganic mineral aggregate, especially for the silica-rich granites. For modification with the amine-based anti-stripping agent, the improvements in water resistance were impressive for both limestone and the second granite, but given the very poor performance of the unmodified bitumen–granite joint, then the use of this amine-based adhesion promoter was shown to be especially effective for this system. Finally, the styrene-butadiene-styrene (SBS) block copolymer was added to the bitumen for use in the bitumen–limestone joints. Not only was the water resistance improved dramatically but also the fracture performance of the dry, unexposed joints were enhanced significantly with an increase in the dry fracture energy from 619 J/m^2 to 1334 J/m^2 being observed.
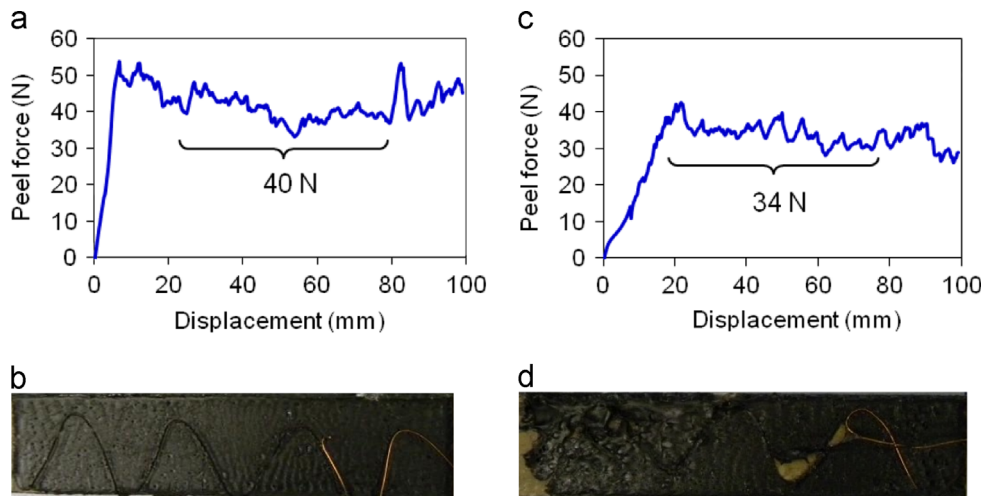
Fig. 9. Peel curves and images of the aggregate fracture surfaces using SBS-modified bitumen binder with limestone aggregate: ((a), (b)) dry specimen; ((c), (d)) water immersed for 3 days.
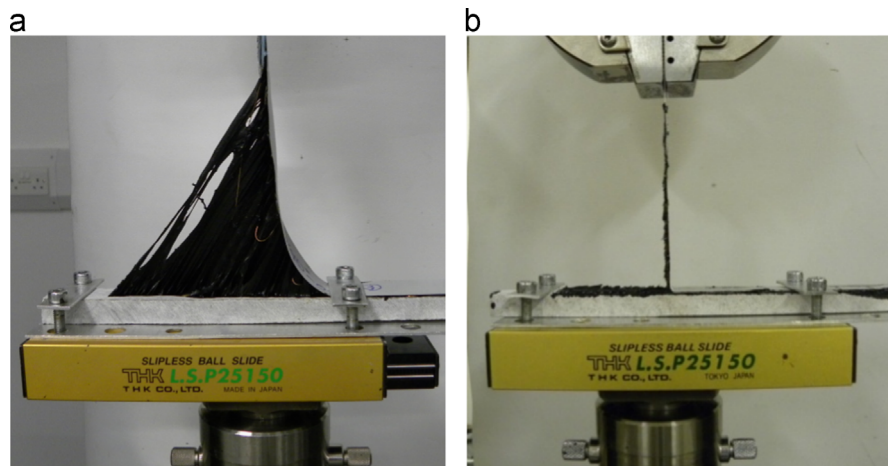

Fig. 10. Peel testing of dry specimens: (a) SBS-modified bitumen; (b) 40/60 pen bitumen.

Acknowledgements

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