Adhesion properties of Warm-Modified Bituminous Binders (WMBBs) determined using Pull-off tests and Atomic Force Microscopy

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**Abstract**

The aggregate-binder bond is one of the main factors that affect the durability of asphalt mixtures. This can be investigated based on the energy required to fracture the adhesive bond between binder and aggregate. In this study, the effects of Sasobit, Rediset WMX and Rediset LQ on the adhesive bond strength of an aggregate-binder system is investigated using the pull-off test. Test data are compared with the nano-scale adhesion force determined using atomic force microscopy (AFM) using the PeakForce Quantitative Nanomechanical Mapping (PFQNM) method. The impact of warm mix additives, test temperature and binder grade on the practical work of fracture was investigated. It was found that Sasobit, Rediset WMX and Rediset LQ increased the practical work of fracture by 170%, 100% and 143% respectively for the aggregate-binder system produced using 40/60 Pen binder, and 70%, 25% and 50% respectively for the system produced using 100/150 Pen binder. The contribution of warm mix additives in improving the practical work of fracture has been linked to the adhesion force determined using AFM. AFM offers great advantage in characterizing the nano-scale properties which were shown to include co-localisation of nano-topography with adhesion, ease of sample preparation and reduction in experimental time relative to the direct tension pull-off test.

Keywords: Adhesion, Sasobit, Rediset, AFM, PFQNM and Pull-off test

**1. Introduction**

The aggregate-binder bond is one of the main fundamental properties affecting the overall performance of asphalt mixture. Different techniques to evaluate aggregate-binder adhesion properties have been developed based on the pull-off test concept. The Pneumatic Adhesion Tensile Testing Instrument (PATTI) was developed by the National Institute of Standards and Technology (NIST) to assess the adhesive bond strength between aggregate and binder taking into account the presence of moisture. This technique was used by Kanitpong and Bahia (2003, 2005) to measure the mechanisms of moisture damage based on the ASTM D4541 (Standard Test Methods of Coating Using Portable Adhesion Testers). Copeland (2007) modified the procedure for preparing PATTI samples by introducing a device to compress the specimens, which enables better control of the bitumen film thickness.

Failure in an aggregate-binder system can possibly occur in two different locations: through the bulk of the asphalt binder, i.e. cohesive failure, or along the interface between the asphalt binder and aggregate, which is known as adhesive failure (Howson 2011). The latter has been conceptually equated to the energy required to fracture the adhesive bond between aggregate and binder. Surface free energy (SFE) is another technique used to evaluate adhesion characteristics between aggregate and binder. SFE methods have been used by Howson *et al.* (2012) and Kringos *et al.* (2008) who found that practical work of fracture is predominantly higher than that predicated from surface energy measurements.

A relationship between ideal work of fracture based on SFE and practical work of fracture was studied by Howson (2011) and Masad *et al.* (2010). These studies are very beneficial in understanding the mechanisms and factors that govern the fracture behaviour of asphalt binders and mixtures through the use of an experimental pull-off test on aggregate-binder systems that allows direct tension force and displacement to be recorded. Despite the usefulness of the direct tension test, these authors reported practical difficulties in preparing aggregate samples, ensuring consistent binder film thickness and in performing the test itself. Other researchers have investigated the adhesive strength bond using similar direct tension tests (Kringos *et al.* 2008, Jakami 2012). It was found that a transition from adhesive to cohesive failure occurred as the binder film thickness increased and the practical work of fracture increased with loading rate and decrease in temperature. A similar conclusion was reported by Al-Haddad and Al-Khalid (2015) who also confirmed that, as film thickness increased, the failure mode transitioned from adhesive to cohesive. These authors also found that, for a complete adhesive failure to occur, binder film thickness between the two aggregate stubs should be equal to or less than 16$ μ$m.

AFM has also been used by number of researchers to investigate topographical structure of bitumen and the effect of short- and long-term ageing on the morphological microstructure of bitumen and polymer-modified bitumen (Allen *et al.* 2012,Das *et al.* 2014,Wu *et al.* 2009,Zhang *et al.* 2011,Zhang *et al.* 2012,Menapace *et al.* 2015). However, very limited studies map the mechanical properties of asphalt binder. Lyne *et al.* (2013) used PeakForce Quantitative Nanomechanical Mapping (PFQNM) modality to investigate the elastic modulus and adhesion of neat bitumen. With this method, the adhesion of bitumen is evaluated based on the attractive force between the probe and the sample. Van der Waals’ forces and electrostatics were considered as contributing factors to the adhesion force between probe and bitumen surface (Pittenger *et al.* 2010). Nazzal and Abu-Qtaish (2013) and Nazzal *et al.* (2015) studied the effect of some warm additives on the nano- and micro-strucaul as well as the adhesive and cohesive properties of an asphalt binder

AFM has the potential, as a powerful research technique, to be used by pavement technologists in investigating the nano-mechanical properties of film asphalt binders. In the current study, the effect of warm additives on binder adhesion was investigated by AFM, and order to link and validate the contribution of warm additives in improving the adhesion performance of bituminous binders at nano-scale to their effect on traditional approaches, a comparison has to be made with practical work of fracture measured using a direct tension pull-off test.

**2. Materials and methods**

***2.1 Materials***

Two binder grades and three warm mix additives are used in this study. Granite was delivered in rocks of approximately 8-10 kg each. Two asphalt binders, namely 40/60 and 100/150 were used. It should be noted that the recommended dosages of Sasobit, Rediset WMX and Rediset LQ which were adopted in this study are 2%, 2% and 0.5% by the weight of the bitumen respectively. For brevity, the binder grades of 40/60 and 100/1500 are named H and S respectively, while the warm mix additives are named based on the first two letters of the word: Sa, Rw and Rl for Sasobit, Rediset WMX and Rediset LQ respectively.

***2.2 Methods***

*2.2.1 PFQNM-AFM*

In AFM, all testing was conducted with a Bruker Multimode atomic force microscope, AFM (NanoScope VIII, Bruker Nano Inc., Nano Surfaces Division, Santa Barbara, CA) equipped with a 150 x 150 x 5 μm scanner (J-scanner) operated with PeakForce Quantitative Nanomechanical Mapping (PFQNM) modality. All tests were conducted at 22$°$C using a Bruker TAP150A probe. TAP150A is a silicon nitride tip with a nominal tip radius of 8 nm and a 5 N/m spring constant. The exact spring constant was determined using the Thermal Tune method and the tip radius was calibrated with a standard Vishay Photostress coating (PS1) polymer (Heilbronn, Germany) of known elastic modulus, 2.7 GPa. The exact spring constant and tip radius after calibration were 5.155 N/m and 9 nm respectively. Force mapping was conducted as follows: the sample was oscillated in the z-direction at 2 KHz at the same time as the sample was moving in the x-y directions at a rate of 0.766 Hz. Each image was composed of 384 x 384 pixels/line. Data was measured over 10x10 $μm$ scans. Data was analyzed off-line using Bruker Nanoscope Analysis software v 1.5.

Data obtained with this AFM method include topography, adhesion force, elastic modulus and deformation. This paper focusses on the adhesion data. All data are presented as an average of five images and the error bars presents standard deviation.

*2.2.2 Pull-off test*

Testing of the aggregate-binder system samples was conducted using a servo hydraulic frame, Instron machine. The Instron machine’s software controlled the operation of the testing machine and recorded loading rate, force, and displacement. The entire testing process was conducted inside an environmental chamber that controlled the test temperature. Custom-designed stainless steel grips were used to hold the sample holders. The upper grip was attached directly into the load cell, while the lower grip was attached to the base of the testing chamber by means of a locking silicone-stainless steel joint that served the purpose of aligning the top and lower grips. A prepared aggregate-bitumen system was fixed into the bottom grip. A servo hydraulic frame was used to apply force while displacement of the thin binder film was measured directly using the Series IX Automated Materials Testing System version 5.28 software. Testing temperatures were 10°C and 20°C in order to investigate their effects on the failure mode. The deformation rate for testing all samples was 25mm/min. Three samples of the aggregate-binder system were tested.

**3. Sample preparation**

***3.1 Warm-modified bituminous binders (WMBBs)***

The modified asphalt binders were prepared as reported by (name deleted to maintain the integrity of the review process). For the preparation of the AFM samples, the heat-cast method was used over the solution cast method in order to avoid the solvents having an effect on the binder composition. Firstly, a metal disc of 15 mm in diameter and 0.88 mm in thickness was placed on a sheet of glass of 300×300×10 mm. The metal disc was heated using a heat gun and then a small amount of heated bitumen which was heated in oven maintained at temperature of 140°C, was cast on it. The heat gun was then used to continue heating the bitumen samples and prepare samples with thickness varying between 100 μm and 500 μm measured using a Vernier calliper.

Three samples were prepared for both the virgin bitumen and the warm-modified bitumen. Five images were captured, for both the virgin and the modified bitumen.

***3.2 Aggregate-binder system***

At the first stage, the rock was cut into sheet plates of uniform thickness (20–40 mm) using electrical sawing. Then, aggregate fingers of approximately 20-40mm height and 12mm diameter were cored from the sheet plates using an electric coring machine with continuous water feed. Aggregate fingers were then cut to aggregate stubs of 12mm diameter and 18mm height using a small cutter. In fact, having a large contact area can increase the probability of cavitation (Al-Haddad and Al-Khalid 2015); therefore, a decision was made to choose a small contact area, in order to reduce the possibility of cavitation occurring.

Both surfaces of the aggregate stubs were then polished using silicon carbide abrasive paper discs. Firstly, both surfaces were polished using 80 silicon carbide abrasive paper in order to adequately level both faces and remove any edges caused when cutting the aggregate fingers. The polishing process was then continued for one face; this process comprised two stages using silicon carbide abrasive paper discs of 120 and 180 respectively, in order to obtain a relatively constant surface roughness so that there were no gaps when using the DSR. Dust which might have been caused by the sawing and drilling process and polishing powder was removed by cleaning the aggregate stubs by immersing them in distilled water, which was boiled for 15 min, and then drying them with hot air. The finished aggregate stubs were placed in an oven for 12 hours at 150$°$C to remove all moisture from them.

Modifications were made to the upper and lower plates of the dynamic shear rheometer (Kinexus DSR Pro+). In addition to that, aggregate stub stainless steel holders were also manufactured to be integrated into those modifications in order to fix the aggregate stubs in the proper position, as presented in Figure 1-A. The aggregate stub holders were firstly aligned in the upper holder and lower plate of the DSR. The aggregate stubs were conditioned overnight in an oven maintained at a temperature of 150$°$C while the control and WMBBs were heated up to 150$°$C prior to setting. The preparation of the aggregate-binder system involved the following: firstly, two heated-aggregate stubs were aligned in the aggregate stub holders, and then a zero gap setting was made between the two stubs. After that, a small drop of binder was applied to the surface of the bottom aggregate stub. Thirdly, the gap was then reduced to the desired film thickness (16$μm$) as recommended by Al-Haddad and Al-Khalid (2015) and the sample was allowed to cool for 15 minutes before the excess binder was removed by means of a sharp knife. The prepared aggregate-binder samples were kept in a controlled temperature fridge maintained at a temperature of 10$°$C for 24 hrs to achieve full adhesive bond. The aggregate-binder system was then aligned in the test aggregate-binder system holders in order to obtain perfect alignment, as shown in Figure 1-B which were manufactured in order to install the aggregate-binder system within the test machine inside controlled environmental chamber, as illustrated in Figures 1-C and 1-D respectively.

**4. Results and discussion**

***4.1 Adhesion characterization obtained from PFQNM-AFM***

Figure 2 shows topography images obtained for the control and warm-modified bituminous binders. As reported by other researchers, the microstructure of bitumen consisting of the peri phase and para phase can be clearly seen in these figures (Loeber *et al.* 1998,Masson *et al.* 2006,Menapace *et al.* 2014). As can be seen in Figure 2-A, the peri and para phases can be clearly seen. However, more importantly, the catana phase does not exist, because the source of those types of binder is Venezuela, and they are classified as a non-waxy bitumen (Das *et al.* 2013). Therefore the catana phase or the bees cannot be observed in the control binders. As Sasobit and Rediset WMX contain wax in their structures, once they were added to the control binders, the catana phase was recognized, as can be seen in Figures 2-B, 2-C, 2-F and 2-G. The effect of Sasobit and Rediset WMX is clearly noticeable. In comparison with the control binders, the peri phase is considerably larger and the para phase is significantly reduced and disappeared in the majority of the scans. The significant change in the topography caused by Sasobit and Rediset WMX may be due to increasing the mobility of the different molecular species within the binder because of the presence of wax. Interestingly, it was noted that Rediset LQ had no any effect on the topography of the control binders and the structure of the peri and para phases remained constant.

 Figure 3 shows the adhesion maps of virgin and warm-modified binders. It can be noticed that the phases of virgin binders exhibited different adhesion values. The adhesive force of the para phase is higher than the adhesive of the peri phase for both 40/60 and 100/150 binders. However, there was a significant increase in the adhesion force of the overall bitumen surface, which can be seen in Figures 3-B, 3-C, 3-F and 3-G, regardless of binder type. Sasobit is classified as a viscosity reducer, and it was not expected to affect the adhesion characterization of bitumen; however, it showed positive improvements in terms of adhesion. The adhesion performance of Sasobit in the current study agrees with what was reported previously by Nazzal and Abu-Qtaish (2013). Sasobit is a fine crystalline, hydrophobic and long chained aliphatic hydrocarbon, therefore, the addition of this additive to an asphalt binder causes the binder to be more hydrophobic which can result in improving the adhesion between aggregate and binder but the reason should be further investigated. The current study recommends Sasobit as an active adhesion enhancer to increase the quality and serviceability of flexible pavements. More importantly, the tolerance dosage of Sasobit should be further investigated with binders that have different dosages of wax in their structures to reach an accurate conclusion.

Rediset WMX exhibits the same trend as Sasobit. Rediset WMX increased the adhesive force by approximately double, while there was less improvement in the adhesive force of Rediset LQ-modified bitumen, as shown in Figures 4-A and 4-B.

***4.2 Adhesion characterization obtained from Pull-off test***

*4.2.1 Analysis of failure mode*

As defined previously, adhesion in the context of asphalt mixture is defined as the attraction force between aggregate and binder/mastic. In other words, it is the required energy to break the bond between aggregate and binder. By contrast, cohesion is defined as the intermolecular force developed within the binder/mastic.

Lytton (2004) studied the relationships between film thickness and failure mode using micromechanics and reported that the transition from adhesive to cohesive occurs at film thickness of less than 100μm. However, a study conducted by Jakami (2012) observed that the transition from adhesive to mix and cohesive or complete cohesive failure occurs at film thickness of 200μm; however, he applied a factor of safety to cover the worst-case scenario that might possibly occur, so he suggested that the transition from adhesive to cohesive occurs at film thickness of 100μm. However he also mentioned that the thickness of the binder/mastic across the actual pavement structure varies considerably, and is generally within the range of 15µm to 40µm and both adhesive and cohesive failure may occur, with one of them perhaps being dominant. Howson (2011) and Masad *et al.* (2010) used image analyses software ImageJ in order to calculate the grey intensity of the surface to assess the total percentage area of adhesive failure, which was found to be in the range of 5% to 45%. The range is too low to be considered as sufficient for the occurrence of the adhesive failure mode (Al-Haddad and Al-Khalid 2015). Al-Haddad and Al-Khalid (2015) used image processing coded in MATLAB to estimate the predominant type of failure for aggregate-binder systems prepared using four types of bitumen and two types of aggregate tested at different temperature levels, loading time and binder thickness. They recommended that, at binder thickness equal to or less than 16μm, the percentage area of adhesive failure is more than 75% for the four types of binder grade and two types of aggregate. In the current study, as mentioned previously, it has therefore been decided that the binder thickness for all control binders and WMBBs should be 16μm.

In fact, there is a simple method to judge whether the type of failure is cohesive or adhesive, based on the shape of loading verses displacement. All WMBBs using 40/60 Pen and the control tested at 20$°$C exhibited complete adhesive failure, as presented in Figure 5, while, when WMBBs using 100/150 were tested at 20$°$C, as shown in Figure 6, the failure mode was mixed adhesive and cohesive, although the binder thickness was 16μm in both scenarios. The reason for this phenomenon is because, the viscosity and stiffness of 40/60 binder are high, so the stored energy in the bitumen is higher than the stored energy along the interface between aggregate and binder; therefore, the failure occurs at the interface between aggregate and binder. In other words, testing the control 40/60 and warm-modified binders at 20$°$C did not allow enough time for the cohesion force between the binder molecules to work and aid in tensile-strength resistance consequently, the resistance process will depend on the adhesion strength between aggregate and binder. Whereas, when control binder 100/150 and warm-modified binders were tested at 20$°$C, the viscosity and stiffness were relatively low, so the deformation rate works further between the bitumen molecules due to the viscos effect, which resulted in decreasing the tensile load and increasing displacement at failure. However, when the testing temperature for the aggregate-binder system using 100/150 Pen and WMBBs was 10°C, the failure mode transitioned from cohesive to adhesive.

A judgement on the failure mode using a load-displacement curve can be made based on the crest of the curve. In complete adhesive failure, the load approaches the maximum value in one point and then after failure the load will drop significantly to zero value. Whereas, in the case of cohesive failure, as the work will be between the binder molecules, the load will take in a steady state while the viscous effect increases the displacement until failure. Figure 5 show typical adhesive failure for the aggregate-binder system using 40/60 Pen and 100/150 Pen tested at 20$°$C while Figure 6 illustrates typical cohesive failure for the aggregate-binder system using 100/150 Pen tested at 20$°$C.

*4.2.2 Practical work of fracture*

The practical work of fracture was calculated based on Harvey and Cebon (2005). The value of the required tensile energy to produce failure could be determined by calculating the area under the curve of tensile load versus displacement. Figure 7 presents the practical work fractures for control binder 40/60 and WMBBs. It was found that the failure mode for all these aggregate-binder systems tested at 20$°$C was adhesive. All warm additives increased the required energy to break the adhesive bond strength between aggregate and binder. Sasobit significantly increased the tensile load which results in increasing the practical work of fracture. In other words, it improved the adhesive bond strength between aggregate and binder. Rediset WMX and LQ also improved the bond strength energy. It is therefore clear that the inclusion of Sasobit and Rediset gives a superior performance in providing an asphalt mixture that has better performance than traditional HMA.

There is no doubt that the test temperature is a crucial parameter affecting the failure mode. Figure 8 shows the required practical work of fracture to break the aggregate-binder bond for aggregate-warm-modified binders produced using 100/150 binder. In this scenario, although the practical work of fracture of aggregate-WMBBs is equal to or better than that of the control, it was found that the failure mode between aggregate and binder was either mixed cohesive and adhesive or complete cohesive failure due to the viscous effect of those binders, so more energy was dissipated in the bulk of the viscoelastic control and warm-modified binders. The failure mode was noticed in the load-displacement curve and by observation, as mentioned previously. It can be concluded that the binder grade highly affects the testing temperature of the bond strength of an aggregate-binder system. The effect of testing temperatures is in agreement to with what was reported by Al-Haddad and Al-Khalid (2015) and Howson *et al.* (2012). However, as the testing temperature decreased to 10$°$Cfor the aggregate-WMBBs system produced using 100/150 binder, all the failure modes were adhesive. Figure 9 illustrates the required energy to fracture the adhesive bond between binder and aggregate, causing isolation from each other, for the aggregate-WMBBS system produced using 100/150 binder tested at 10°C. It can be observed that the rank performance of improving the practical work of fracture using Sasobit and both types of Rediset is exactly the same after taking the effect of testing temperature and binder grade into account.

In general, in both scenarii of testing the aggregate-WMBBs system produced using 40/60 binder at 20$°$C and testing the aggregate-WMBBs system produced using 100/150 binder at 10$°$C, Saobit, Rediset WMX and Rediset LQ increased the required practical work of fracture by 170%, 100% and 143% respectively for the aggregate-binder system produced using 40/60 binder, and 70%, 25% and 50% respectively for the aggregate-binder system produced using 100/150 binder. All data are presented as an average of three samples and the error bars presents standard deviation.

***4.3 Comparison between adhesions obtained from Pull-Off test and AFM***

Based on the obtained results, the performance of warm additives in improving the practical work of fractures is qualitatively associated with the measured adhesion force determined using PFQNM. Table 1 illustrates the performance of warm additives using both techniques. the adhesion measurement of nano-scale properties of WMBBs determined with PFQNM was conducted at 22$°$C and the effects of Sasobit and both types of Rediset were exactly the same on control binders 40/60 and 100/150. However, when using the pull-off test, it was not possible to obtain the same rank performance of the warm additives on both control binders for the aggregate-binder system tested at 20$°$C because the failure mode of the aggregate-WMBBs system using 100/150 was a mixture of cohesive and adhesive. However, as all the measurements of the aggregate-binder system produced using 100/150 were conducted at 10$°$C, the effect of the warm additives was equivalent to what was noticed when using 40/60. In other words, the effect of testing temperature and binder grade on the failure mode is clear. This finding may be one of the advantages of using AFM to directly characterise the adhesion of binders. Other advantages of using AFM to characterise adhesion are ease of sample preparation and reduced experimental time relative to the pull-off test.

**5. Conclusion**

The bond strength between aggregate and binder/mastic plays a major role in the overall performance of an asphalt mixture. In this study, the effect of warm mix additives on the bond strength of aggregate-binder systems was investigated in detail. Furthermore, a comparison was made between the practical work of fracture and the attraction adhesion force between the probe and binder surface using Atomic Force Microscopy. The main findings of the study are:

1. It was found that Sasobit, Rediset WMX and Rediset LQ increased the practical work of fracture by 170, 100 and 143% respectively for the aggregate-binder system produced using a 40/60 Pen binder, and 70, 25 and 50% respectively for the aggregate-binder system produced using a 100/150 Pen binder.
2. It was possible to obtain complete adhesive failure for the aggregate-binder system using 40/60 Pen tested at 20°C but not with the 100/150 Pen at the same temperature and binder film thickness. The reason was attributed to the mode of failure being mixed cohesive and adhesive, or at times complete cohesive failure. Therefore, control and warm-modified binders using 100/150 Pen were tested at 10°C. The failure modes were noticed visually and confirmed by the shape of the load-displacement curve.
3. After taking into account the effect of test temperature on the adhesive bond in aggregate-binder systems produced with 40/60 and 100/150 Pen binders, it was evident that the effect of Sasobit and both types of Rediset is exactly the same: they all improved adhesion.
4. Sasobit was also found to improve the bitumen cohesion characteristics; it can therefore be suggested that Sasobit could be used as an active adhesion enhancer to improve aggregate-binder bonding. It was shown that both Rediset WMX and LQ improved the adhesion characteristics of warm modified bituminous binders by around 110% and 50% respectively using PFQNM.
5. The impact of warm mix additives on the practical work of fracture for aggregate-binder systems was qualitatively correlated with their effect on the adhesion force determined using PFQNM.
6. The main advantages of using AFM to characterize nano-scale properties were shown to include co-localisation of nano-topography with adhesion, ease of sample preparation and reduction in experimental time relative to the direct tension pull-off test.

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