A Benchmarking Study of Anionic Bitumen Emulsion Properties for Slurry Seals

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***Synopsis*—Bitumen emulsions are the most commonly used bituminous products for roads in Southern Africa because they are relatively inexpensive to apply, in comparison with hot bituminous binders. Although there have been great strides taken in the improvement of bituminous emulsions for slurry seals through the years, current specifications and testing procedures are empirical and not related to common service failures. The quality of a bituminous emulsion is affected by the rheological properties of the base binder, particle size and formulation ingredients, which in turn affects its in-service performance. Several potential performance related test methods for emulsions have been developed over the years. This paper evaluates the properties of South African anionic emulsions with these performance-related tests and the current empirical tests. This paper aims to show the possible limitations of empirical tests in analysing bituminous emulsion properties and the need for better characterisation methods to overcome current performance challenges.**

***Keywords*— anionic bitumen emulsion; performance properties; rheology**

I. Introduction

Bitumen emulsions are one of the most cost effective and energy efficient materials used for road construction and maintenance [1]. They can be defined as a mixture of water and bituminous binder in the presence of an emulsifier. Emulsions are versatile and are used in various applications such as tack coats, prime coats, fog seals, slurry seals, chip seals, cape seals etc. Slurry seals are the most commonly used type of surfacing in South Africa. The function of a bitumen emulsion in a slurry seal is to bind the aggregate on the road and seal the underlying structural layers from moisture intrusion. Common slurry seal failures relate to the properties of the binder (from either bitumen emulsion or hot bituminous binder application) and they include ravelling and bleeding. It is therefore important that specifications are able to identify emulsions that will give maximum resistance to ravelling and bleeding.

Current guidelines and specifications for bitumen emulsions for use in surface treatment are contained in SABITA Manual 10, which is dedicated to surface seals and laboratory tests for their classification, and appropriate surface treatment to use in various conditions [2]. Anionic emulsions are commonly used emulsions in South Africa as they are suited for both hot and dry conditions [2]. However, current test methods and specifications for emulsions remain largely empirical and not related to distresses observed in the field; besides the progress made in the development of high performing emulsifiers [5]. Several studies [3-5], [8] and [10] have reported on the potential performance-based tests for bitumen emulsions and their residues. The main objective of this paper is to evaluate the properties of anionic emulsions used in slurry seals with both conventional and performance related tests, in order to identify possible limitations in the current specifications and test methods.

II. BACKGROUND

A slurry seal is defined as a homogenous mixture of fine aggregate, slow setting bitumen emulsion, cement and water; which is applied on the surface of a pavement (base course, old HMA, or cape seals). The water evaporates leaving behind a final product that resemble a hot mix asphalt. A bitumen emulsion is made up of water, bituminous binder, as well as an emulsifier and, in some instances, other additives. The ingredients are mixed using highly specialised shear equipment, under carefully controlled conditions, to make a stable dispersion of the bitumen in the water phase [8].

The emulsion is expected to remain stable and not coalescence during storage, pumping and transporting. The viscosity of the emulsions must also allow the emulsions to be pumped and sprayed with minimal energy. However, the emulsion is expected to break and cure within a reasonable time after being mixed with aggregate and placed on the road during construction, in order to allow for a fast reopening of the road to traffic [5]. Breaking happens when the bitumen droplets coalesce and water in an emulsion evaporates during curing, leaving behind a bitumen residue that is supposed to have rheological properties similar to the neat binder that was used to make the emulsion [4]. The residual binder is expected to have sufficient cohesive and adhesive strength to bond with aggregates and bind them on the road, under the abrasive force of traffic, to resist ravelling [8]. The residual binder is also expected to have sufficient stiffness to resist bleeding in cases where aggregates are pushed into the existing surface or when soft aggregates break and reduce the volume of air voids in a seal. Bitumen emulsions are classified as anionic, cationic, and non-ionic, depending on the charge imparted on the bitumen droplet [8]. As shown in Fig.1, cationic emulsifiers are typically ammonium compounds that contain positively charged nitrogen (N) atoms in their head group; whereas an anionic emulsifier typically contains negatively charged oxygen (O) atoms. The charged portion of emulsifiers is located at the interface of the bitumen and the water, while the hydrophobic tail is firmly bound in the surface of the bitumen droplet. The charge on the emulsifier keeps the emulsions stable by preventing the bitumen droplets coming close to each other and eventually coalescing [8].

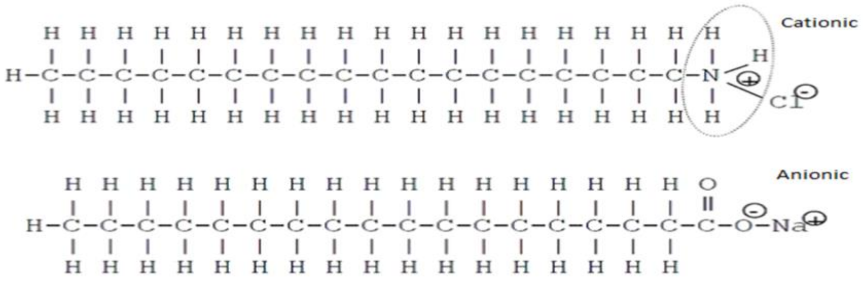

Fig. 1. The cationic and anionic emulsifier [9]

The storage stability of bitumen emulsions is determined by several factors, which include the amount and type of emulsifier, exposure of an emulsion to shearing, storage time and temperature, among others [5]. Emulsions for slurry seals are generally slow-set emulsions which are made with a high quantity of emulsifier compared to rapid-set emulsions used in chip seals. Unstable emulsions break prematurely during storage and they cannot be used any more. Emulsion stability may also affect the ability of the emulsion to be pumped or sprayed uniformly on a pavement surface.

The breaking of the emulsion occurs in different rates depending on the emulsion formulation, the aggregates, as well as the environmental factors such as temperature, wind speed, humidity and mechanical action. The phases that an emulsion undergoes during breaking and setting (as illustrated in Fig.2) can be described as follows [6]:

- Emulsion – The stable emulsion is created, where the droplets are well dispersed with sufficient distance between them.
- Flocculation – The distance between the droplets is not sufficient. This may be caused by destabilizing the emulsion, evaporation of the water phase or mechanical action.
- Coalescence – Having the droplets at close proximity, will have them fuse together. The water that happened to be trapped in the coalesced layer is then diffused out to leave a bitumen residue. Mechanical actions, such as compaction tend to assist in fusing out the trapped water (breaking) [6].

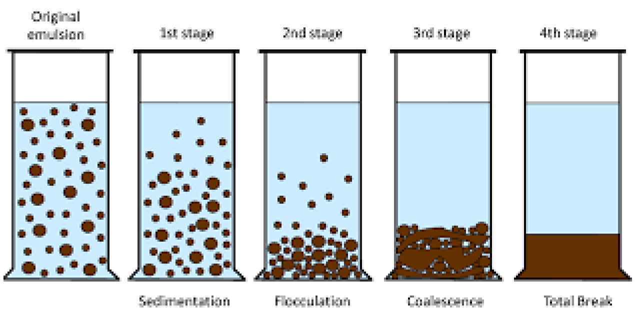

Fig. 2. The different stages of the breaking process of a bitumen emulsion[15]

The breaking process must not happen during storage, but only after field application. It is therefore important to have effective testing methods that can identify emulsions with desirable storage stability properties. Current test methods that evaluate the storage stability of emulsions are contained in SANS 4001-BT3 [18], while a new testing procedure known as the a 3-Step Shear Method was developed by Johannes and Bahia [17] and extensively evaluated in [5] and found to be capable of differentiating emulsions with different storage lives.

Another important property of emulsions is viscosity, which measures the ease with which an emulsion can be pumped or sprayed on a pavement surface. Viscosity can also affect the ability of an emulsion to be mixed with aggregate in the case of emulsions for slurry seals and micro-surfacing or for soil stabilization. Emulsions with high viscosity may result in streaking during spraying while those with low viscosity may drain off the road surface especially at areas with steep gradients [5]. Both streaking and drain-out result in ravelling and should be avoided. Factors that affects emulsions viscosity include the bitumen content, handling and application temperature and the emulsion chemistry [17]. The Saybolt Furol test (ASTM D88) is currently used for evaluating the viscosity of a bitumen emulsion. However, there has been ongoing effort for an alternative test method, such as the use of a rotational viscometer. The ability of a rotational viscometer to determine emulsion viscosity was evaluated at great length in the NCHRP 9-50 [5] and has been reported to be promising.

Once a slurry seal is constructed, the most important properties of an emulsion that affect its in-service performance are the properties of the residual binder. The residual binder must have sufficient cohesive strength to bind the aggregate on the road under traffic loading in order to resist ravelling. Ravelling is a process where aggregates are lost from a surface treatment under traffic loading. Factors that affect ravelling include the rheological property of the binder (including aged properties), binder application rate, residual binder content and binder-aggregate compatibility [5]. Another important performance parameter of a slurry seal is bleeding. Bleeding can be defined as excess bitumen which is squeezed out of the seal on the surface of the pavement under traffic. Bleeding is undesirable because it reduces the skid resistance of a pavement surface and thus making it dangerous, especially during the wet season. Factors contributing to bleeding include the properties and the amount of the residual binder present in the applied layer [5]. However, bleeding can also occur if soft aggregates are used.

Current specifications for bitumen emulsions do not allow for the properties of emulsions that contribute to ravelling or bleeding to be evaluated. However, studies by [3 -5] have shown the Multiple Stress Creep and Recovery Test (ASTM D7405) and the Frequency Sweep (ASTM D7175) to be potential candidates for evaluating resistance to raveling and bleeding.

III. METHODOLOGY

A. *Materials*

Five (5) emulsion types commonly used in slurry seals were obtained from suppliers nationally. The 5 emulsions were assigned codes as E-1 to E-5. Samples arrived in large volumes (≥5L) and upon arrival, samples were gently stirred for between 5-10 minutes, depending on the sample size. They were subsequently decanted into 1L or 2L tins and stored and tested in the CSIR laboratory at temperatures between 23°C-25°C to avoid accelerated separation of the emulsion prior to testing.

The sample preparation was as follows:

- Prior to testing, the decanted samples were again gently stirred for 3-5 minutes to ensure the emulsions had not separated while stored.
- Apart from the emulsion sample used for the residue on sieve test, the rest was passed through the 710µm sieve.

B. *Test Methods Conducted*

The emulsions were subjected to a range of testing. The actual tests carried out are given in Table I and Table II respectively. Table I represents current test methods while Table II represents proposed test methods. The proposed test methods are also graphically summarized in Fig.3.

TABLE I. CURRENT STANDARD TEST METHODS FOR STABLE-MIX (60) BITUMEN EMULSIONS

Description	PROPERTY	TEST METHODS
Storage Stability	Binder Content (% m/m)	ASTM D244
	Sedimentation	SANS 4001-BT3
	Coagulation Value (%)	
	Residue on Sieve (g/100ml)	EN1429 (IP91)

TABLE II. PROPOSED PERFORMANCE TEST METHODS FOR STABLE-MIX (60) EMULSIONS

Tests on Fresh Emulsion Properties		
Engineering Property	**Test Method**	**Parameters Measured**
Handling	Settlement and Sedimentation (Modified ASTM D6930)	• Rotational viscosity, η
Storage Stability		• Rotational Viscosity, η, • Separation ratio (R_s) • Stability Ratio (R_d)
Residue Recovery Method: ASTM D7497 Method B		
Resistance to Rutting	Multiple Stress Creep and Recovery Test (ASTM D7405)	• Non—recoverable Creep Compliance (Jnr) • Stress Sensitivity
Thermal Cracking	Frequency Sweep (ASTM D7175)	• Complex Modulus (G*) at Critical Phase Angle (δ_c)

The performance of surface treatments can be greatly affected by the changes in the properties of the respective bitumen emulsions during the storage, transportation and construction stages. Fig.3 illustrates the identified performance tests and their relation to in-service performance.

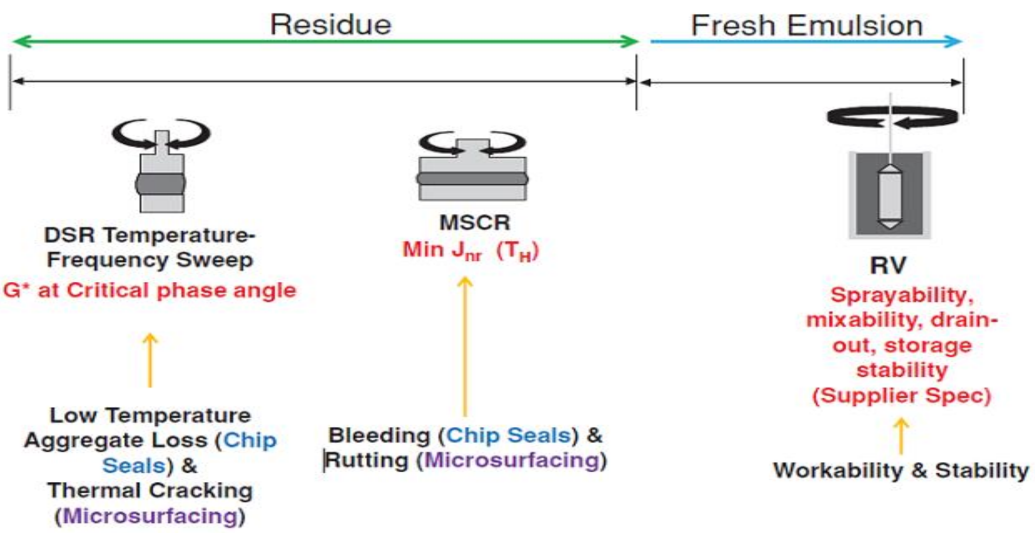

Fig. 3. An Illustration of the Suggested Performance-Related Tests [5]

The experimental plan with the different test methods are given in Tables [III-V].

TABLE III. EXPERIMENTAL PLAN FOR THE STORAGE STABILITY

Factors	Levels	Description
Emulsion Type	5	E-1, E-2, E-3, E-4 and E-5
Storage time	2	1 and 5 days
Test Methods	2	ASTM
Replicates	2	Single operator
Test Temperature	1	25°C
Total	40	

TABLE IV. EXPERIMENTAL PLAN FOR THE MSCR TEST

Factors	Levels	Description
Emulsion Type	5	E-1, E-2, E-3, E-4 and E-5
Temperature	4	46°C, 52°C, 58°C and 64°C
Replicates	2	Single operator
Stress Conditions	1	3.2 kPa
Total	40	

TABLE V. EXPERIMENTAL PLAN FOR THE FREQUENCY SWEEP TEST

Factors	Levels	Description
Emulsion Type	5	E-1, E-2, E-3, E-4 and E-5
Temperature	2	5°C and 15°C
Replicates	2	Single operator
Stress Conditions	1	3.2 kPa
Total	20	

IV. RESULTS

A. *Storage Stability*

The stability of a bitumen emulsion is maintained by the sufficient repulsive forces among the particles, which exist due to the presence of the electrical surface charges [16]. With good stability, a bitumen emulsion can be stored and handled for greater periods of time without prematurely breaking. The anionic emulsion samples provided were tested for storage stability as per current standard test methods in SANS 4001-BT3 (see Table VI) and proposed performance-based methods shown in Table II. The results for storage stability, as per the current standards, are given in Table VI. The results show that apart from one emulsion (E-1), all emulsions failed the storage stability requirement by not conforming to the sedimentation criteria.

TABLE VI. CURRENT STANDARD TESTING FOR STABLE-MIX ANIONIC EMULSIONS

PROPERTY	REQUIREMENTS	SUPPLIERS					TEST METHODS
		E-1	E-2	E-3	E-4	E-5	
Binder Content (%)	60-62	60.4	62.0	61.2	62.1	62.1	ASTM D244
Sedimentation	< 60 Rotations	35	125	85	155	185	SANS 4001-BT3
Coagulation Value (%)	< 2.0	0.0	0.0	0.1	0.0	0.0	
Residue on Sieve (g/100ml)	710µm: < 1.0	0.015	0.019	0.003	0.042	0.061	EN1429 (IP91)
	150µm: < 0.25	0.017	0.021	0.030	0.051	0.050	

The results for storage stability as per the new proposed methods are given in Table VII. In terms of the stability ratio (R_d), the percentage change of the viscosities from the top and bottom layers of the emulsion, at specific conditioning times, all emulsions met the limits stipulated. With regards to the separation ratio (R_s), the change in emulsion viscosity at certain conditioning times and temperature, all but one emulsion (E-4) were within the limits. Using the settlement and stability test, the emulsions showed better short-term (24 hours) storage stability than long-term (5 days) storage stability, as would be expected.

TABLE VII. THE PHYSICICAL AND RHEOLOGICAL STABILITY OF ANIONIC EMULSIONS

PROPERTY	PROPOSED REQUIREMENTS	SUPPLIERS					TEST METHODS
		E-1	E-2	E-3	E-4	E-5	
Storage Stability (25°C, Pa.s)	R_s: 0.2 to 1.5	0.763	0.896	0.247	0.006	0.265	Modified ASTM D6930
	R_d: < 1.5	1.04	0.821	0.829	0.424	0.725	
Settlement and Stability (%)	24 hrs	6.0	8.2	15.4	13.1	19.7	ASTM D6930
	5 days	26.4	41.2	41.4	39.3	50.0	

The results for long-term (5 days storage time) and short term (24 hrs storage time) were plotted against one another and the results are presented in Fig.4. It can be seen that there appears to be a good correlation between the short-term and long-term storage stability results, although one emulsion sample (E-2) was an outlier. However, there is a need to test a variety of emulsions to verify the results in Fig.4. The results for the short-term (24 hrs) and long-term storage stability tests were also plotted against the results from the sedimentation test and the results are presented in Figures 5 and 6 respectively. The results in Fig.5, show a reasonable correlation between the short-term storage stability results and the sedimentation results. On the other hand, Fig.6 shows a good correlation between the long-term storage stability results and the sedimentation results. The latter correlation could justify why the South African specification has existed with just the sedimentation test up until today.

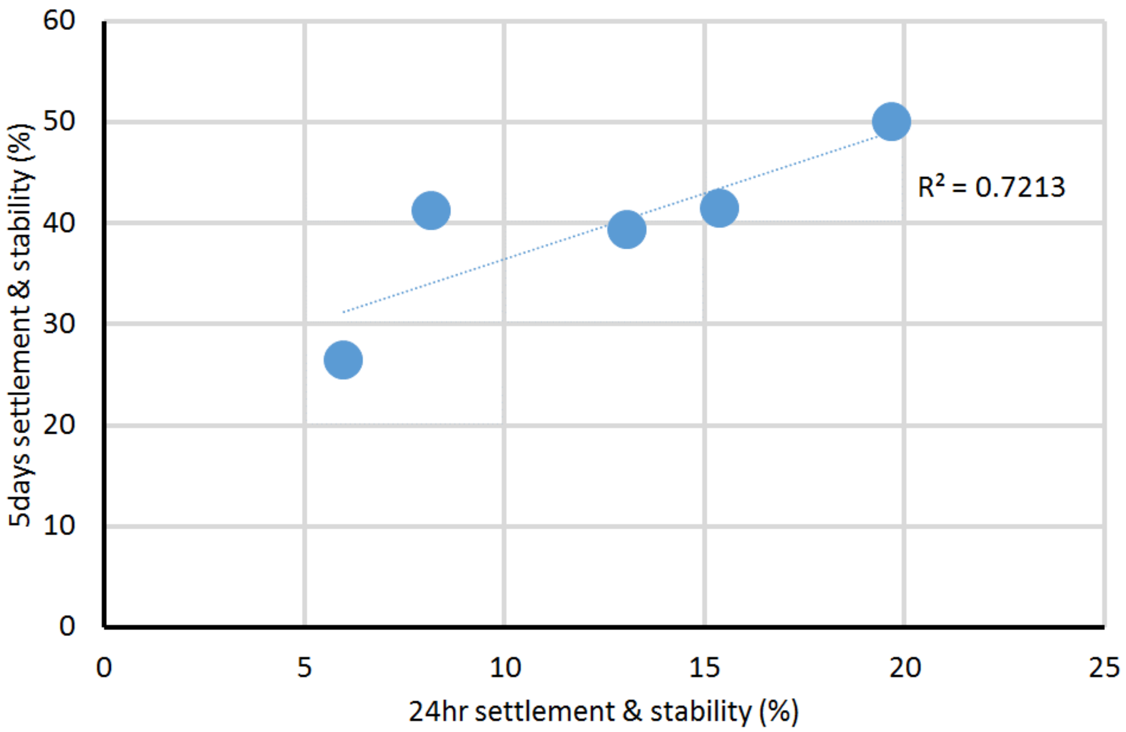

Fig. 4. A correlation between the 5 days and 24 hours settlement and stability results

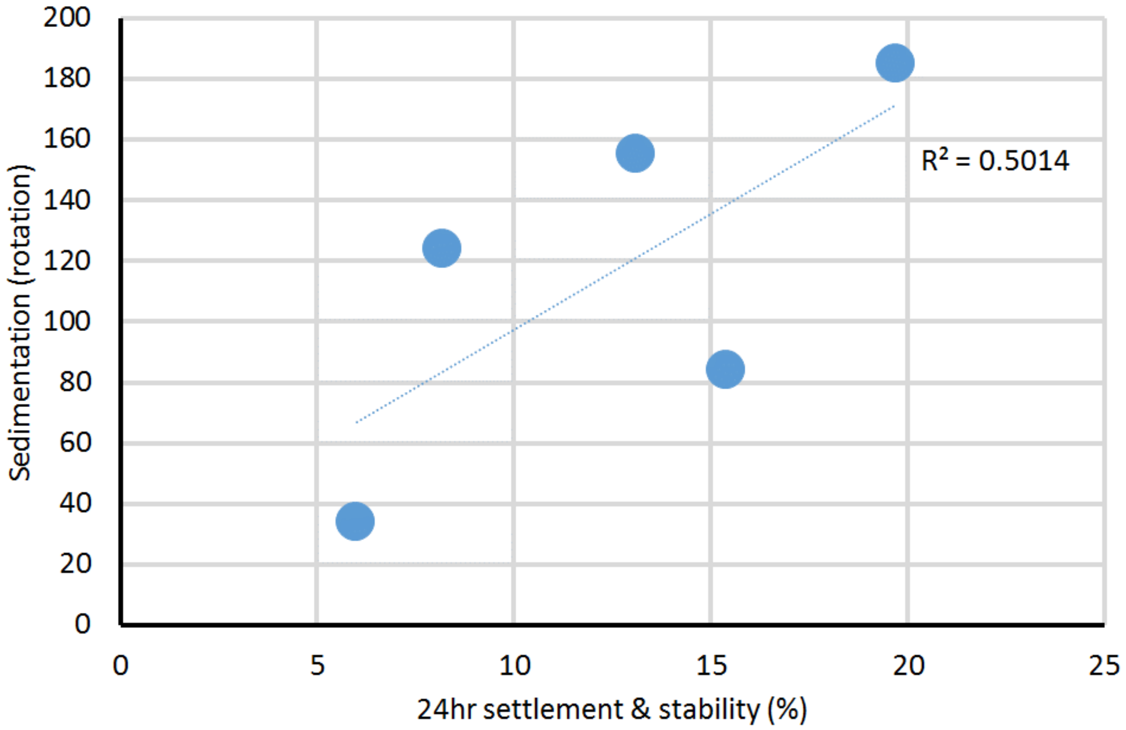

Fig. 5. A correlation between sedimentation and 24 hours settlement and stability results

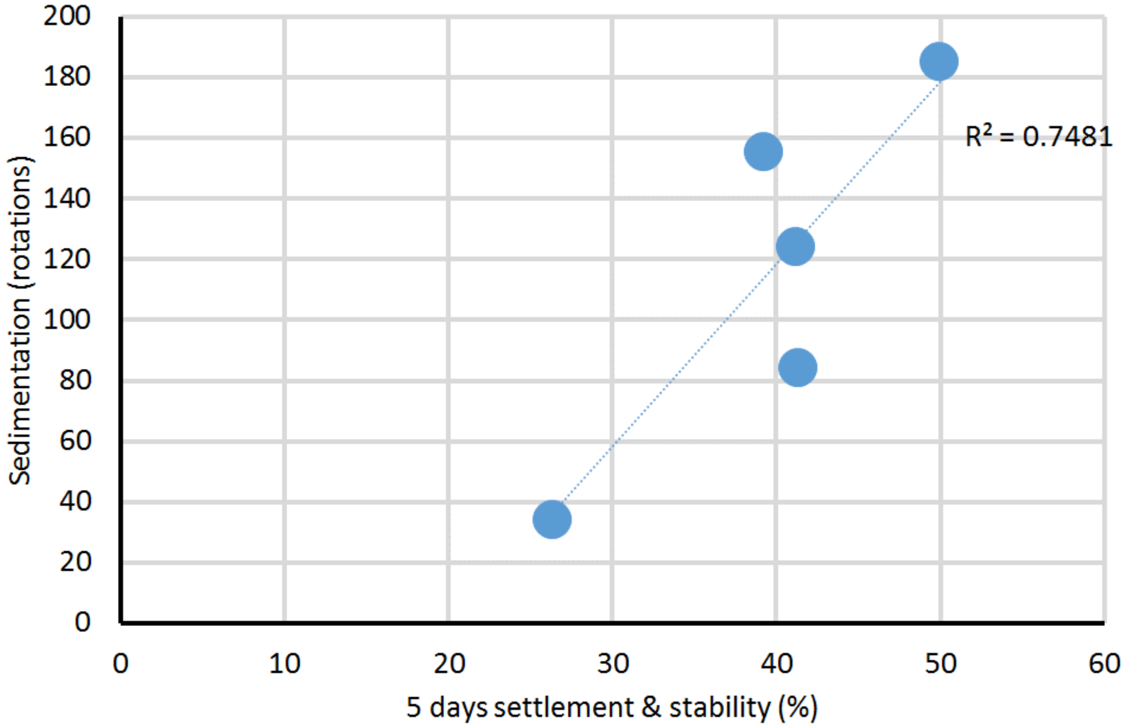

Fig. 6. A correlation between sedimentation and 5 days settlement and stability results

B. *Viscosity*

There are no handling and application criteria for SS60 in SANS 4001-BT3. The specification assumes such a criterion is not useful for these emulsions given they are typically mixed with stone chippings, natural gravels and/or soils, prior to application.

Although spray emulsion viscosity criteria at 50°C are not relevant for these emulsions, an indication of their mixing and handling behaviour at lower temperatures is important. Internationally, this is why a criterion at 25°C is stipulated [17]. Applying this criterion to these emulsions, using DSR obtained viscosities, so as to define an appropriate shear rate for handling and application, resulted in the values shown in Fig.7. Given all tested emulsions had appropriate physical handling attributes, it implies a criterion can be set to ensure future conformance.

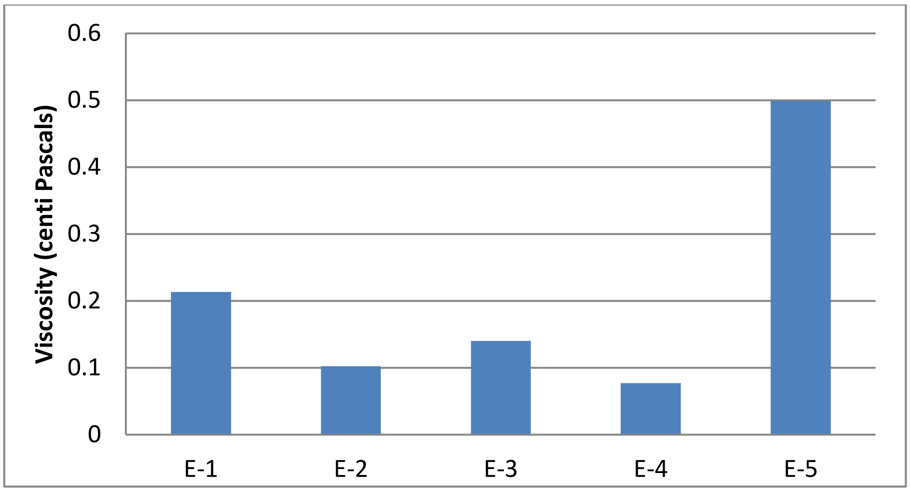

Fig. 7. The Physical and Rheological Stability of Anionic Emulsions

C. *Resistance to Bleeding*

The bleeding resistance of the emulsion residues, using the non-recoverable creep compliance (J_{nr}), was evaluated at the maximum stress level, 3.2kPa^{-1}. The lower the J_{nr} value observed, the better the resistance to bleeding of the residue at a given traffic load and temperature. The results of the emulsions evaluated in this study are given in Table X and Fig. 8. Typically, with an increase in temperature, there was an increase in J_{nr} value, indicating a decrease in the resistance of the residues to bleeding.

Although it is the current practice for emulsions to use the same base binder in South Africa, the variation in J_{nr} of the emulsion residues in Table IX implies that the slurry seal binders belong to different binder classes, if graded as per the current SATS 3208 [19], as shown in Table IX.

TABLE VIII. THE J_{NR} OF THE SLURRY SEAL RESIDUE AT 3.2KPA^{-1}

Temperature (°C)	Jnr @ 3.2 kPa^{-1}				
	E-1	E-2	E-3	E-4	E-5
46	1.32	0.84	0.38	0.58	0.57
52	3.00	2.46	1.14	1.61	1.70
58		6.58	3.05	4.02	4.19
64		15.01	6.93	9.40	9.40

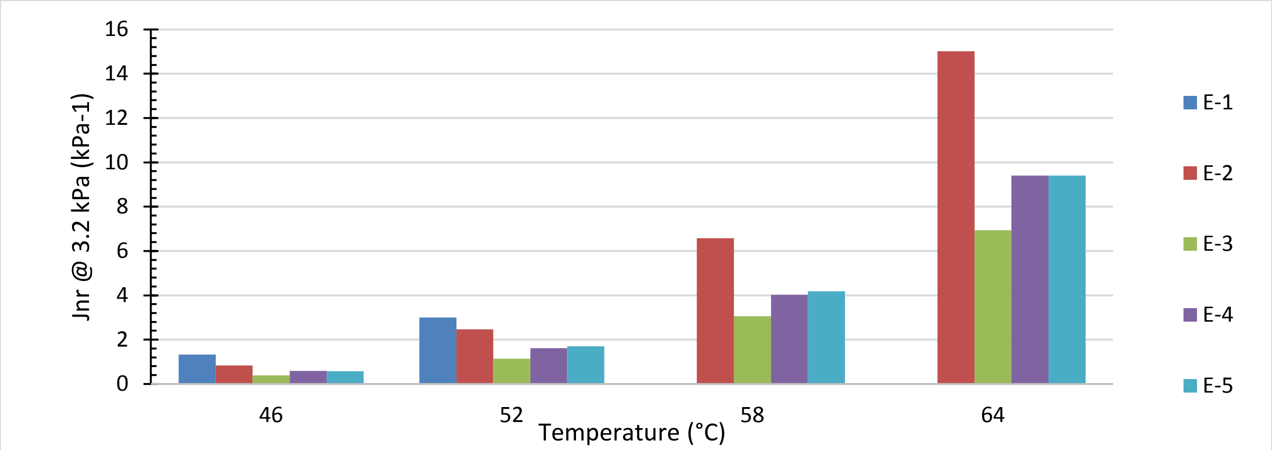

Fig. 8. J_{nr} results at different temperatures for anionic slurry seal emulsion residues

TABLE IX. SOUTH AFRICAN BINDER CLASSES [19]

Binder Classification	J_{nr} limits	Selection for Traffic Condition
S	≤ 4.5	< 10 million ESALs AND Traffic speed > 70 km/h
H	≤ 2.0	10 – 30 million ESALs OR Traffic speed 20-70 km/h
V	≤ 1.0	> 30 million ESALs OR Traffic speed < 20 km/h
E	≤ 0.5	> 30 million ESALs AND Traffic speed < 20 km/h

D. *Thermal Cracking*

Given a slurry seal is used mainly to bind and seal underlying structural layers, its structural capacity is limited and therefore its susceptibility to fatigue or reflective cracking. With ravelling being the primary failure experienced by slurry seals over time, an evaluation of the PAV aged residue is used in identifying the residues' susceptibility to age related ravelling. An evaluation of the performance behaviour of the PAV-aged emulsion residues over a wide range of temperatures, is shown in Fig.9.

The evaluation was carried out at 5°C and 15°C, where the complex modulus at critical phase angle (45°) was evaluated. This modulus, shown in Fig.11, is referred to as the cross-over modulus, where the storage modulus and loss modulus meet, which indicates the point of transition of the residue from a viscoelastic fluid to a viscoelastic solid [18]. A lower cross-over modulus suggests that the residue has a better ability to withstand the loads at low temperatures, because of the 'fluidity' present, which prevents premature cracking.

Fig.10 shows an increase in complex modulus with an increase in the load applied to the residue. There is a wide variation in the values of the cross-over modulus between the emulsion residues, and some have even failed to meet limits advised for thermal cracking parameters for surface applications.

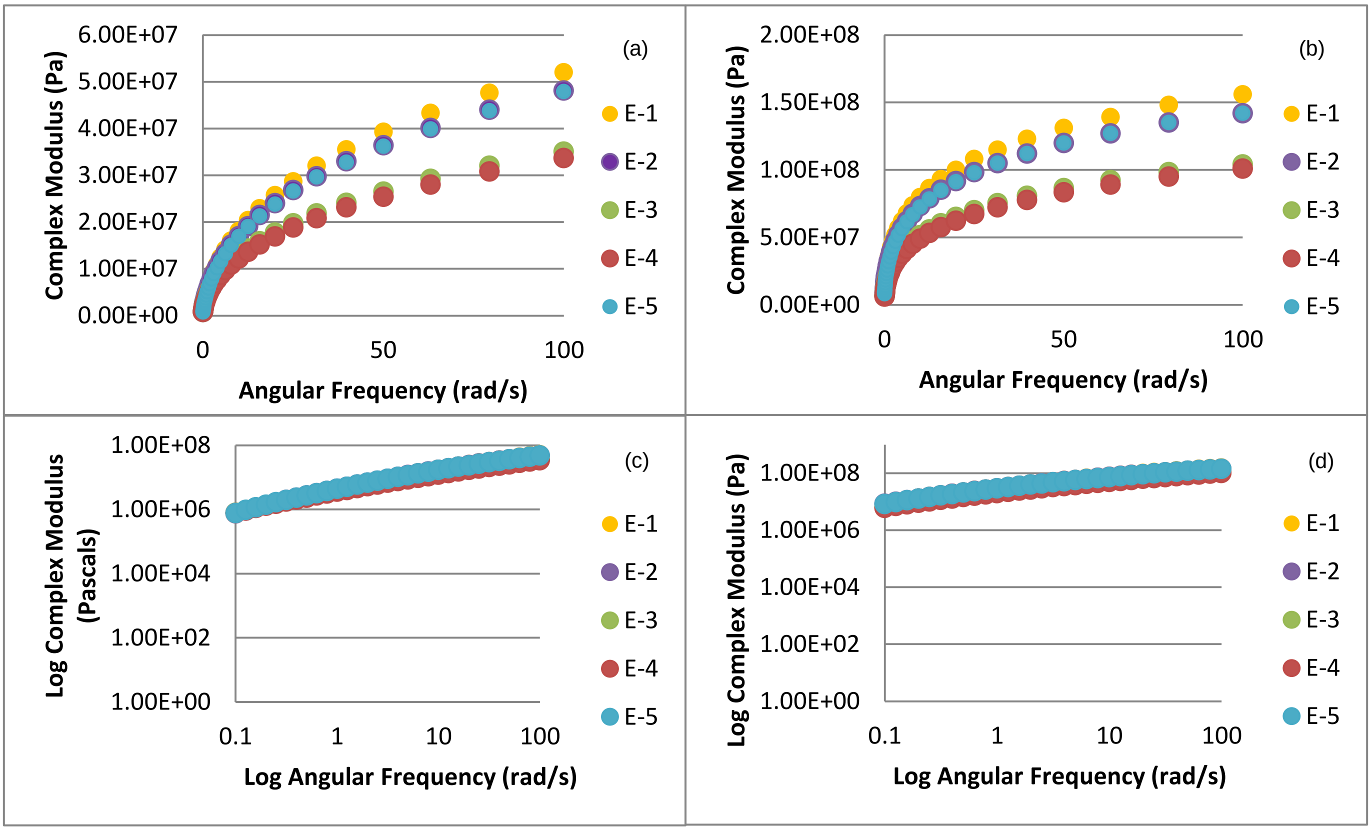

Fig. 9. The Complex modulus of PAV aged emulsion residues at 15°C (a) & (c) and 5°C (b) & (d)

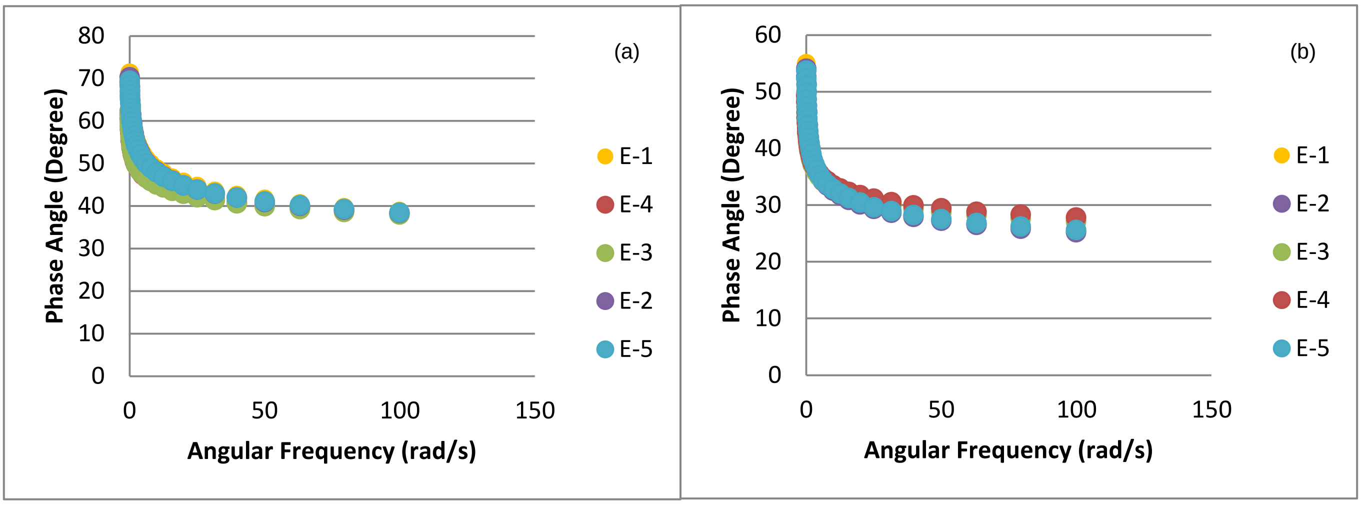

Fig. 10. The phase angle of the PAV aged emulsion residue at 15°C (a) and 5°C (b)

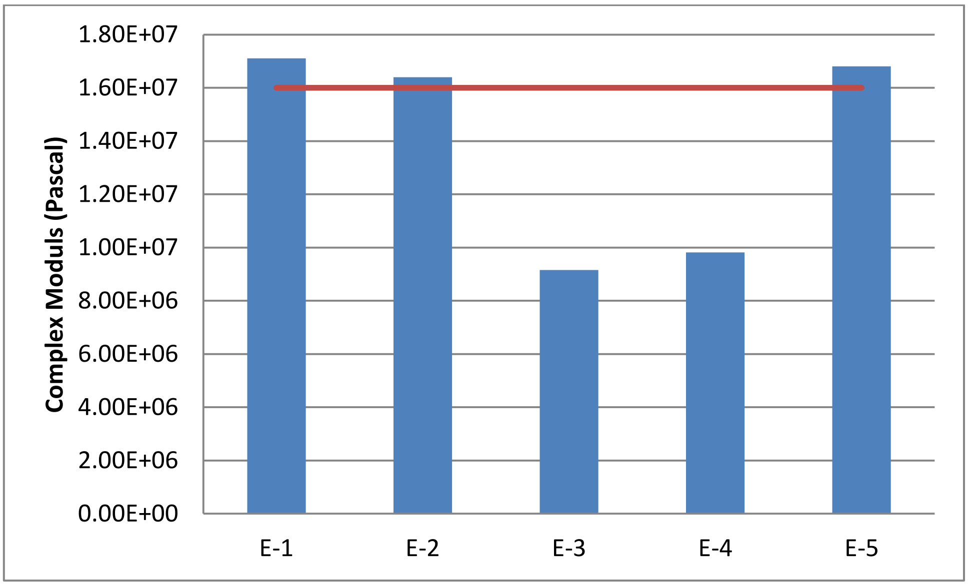

Fig. 11. Complex modulus at the critical phase angle (45°)

V. CONCLUSION AND RECOMMENDATIONS

Although the standard test methods in SANS 4001-BT3 [19] are able to classify bitumen emulsions, the properties included seem either inadequate and/or insufficient for a performance specification. On analysing selected performance-based properties, the following findings were made:

- The stability of anionic bituminous emulsions was shown to vary at short-term and long-term storage times. Only at long-term storage was a reasonable correlation observed with sedimentation results.
- A viscosity criterion could be useful in the specification.
- The J_{nr} values of the emulsion residues imply they would fit into different binder classes, although the typical practice nationally is to use the same grade of base binder. Given rutting performance is dependent on the overall interaction between the aggregate, emulsion residues and other additives, a rutting parameter that incorporates the aggregate contribution could be useful.
- The thermal cracking resistance properties of the emulsion residues showed varied behaviour, with some exhibiting poor and borderline performance compared to the required behaviour of the residues at low temperatures with ageing time.

The variation in results of emulsions of the same grade could be due to a variety of reasons, such as the different formulations used by the different suppliers, or the different manufacturing processes used to make these emulsions. Consequently, the specification and its corresponding test methods need to provide insight into these processes, as well as link test results to the in-service performance of these emulsions.

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