Elongational Rheology of Bitumen Film Samples as a Fingerprinting Technique

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***Synopsis*—The development of improved test methods for modified bituminous binders is currently being pursued at the Council for Scientific and Industrial Research (CSIR). The ductility test laid the initial ground work for all extensional testing of asphalt bitumen in South Africa. However, with time, critical challenges of using this test as a performance indicator for bitumen were identified. As a result, it was withdrawn and equivalent tests, namely the Force Ductility (FD) test, the Binder Yield Energy Test (BYET) and more recently, the Double-Edge-Notched Tension (DENT) test, were brought to South Africa. Depending on the investigated elongational rheological property, each of these tests has their own significance. A major drawback of all the tests is the amount of material needed to determine test properties. This poses a major challenge during forensic investigations into premature failures of asphalt pavements, where extraction and recovery of the *in-situ* asphalt binder often results in insufficient quantity of bitumen for comprehensive characterisation. This paper presents a preliminary study towards overcoming this challenge through extensional methods, whereby thin bituminous films are tested with the Dynamic Shear Rheometer (DSR). Studies in the behaviour of bitumen as a thin film tends to be more representative of the *in-situ* conditions of the binder within an asphalt pavement. Limited results to date have enabled the ranking of different binders according to their transient extensional viscosity as well as differentiated modified from unmodified binders based on the strain hardening effect. Therefore this approach has the potential for improving and replacing current extensional methods in the South African asphalt pavement industry.**

***Keywords*—extensional viscosity, elongational, rheology, strain hardening**

I. INTRODUCTION

The ductility test [1] was once part of the bitumen specification in South Africa. Due to inherent challenges with the method, it was withdrawn and an improved extensional test has been sought after nationally ever since.

The force ductility method was adopted into the national guideline document for modified binders as a potential replacement of the ductility test [2]. Limitations in setting a criteria for this method and the lack of correlation to asphalt fatigue behaviour led to its eventual retraction in 2015. Based on similar challenges, the surrogate dynamic shear rheometer (DSR) method, known as the binder yield energy test, was evaluated but never adopted in South Africa [3]. Such methods are nonetheless still useful for binder identification purposes [4].

In terms of performance predictions, Kandhal [5] correlated ductility results with performance of experimental pavement sections in Pennsylvania, which inspired a wave of research correlating to the conventional ductility parameter. Studies have since shown limitations in the ductility and its surrogate parameters in predicting the behaviour of highly modified binders [6]. Maluke *et al*. [7] recently linked the Double Edge Notched Test (DENT) results to four point bending beam results of asphalt specimen based on both unmodified and modified binders used in South Africa. It reiterated the importance of extensional tests and elongational rheological properties in giving an indication of fatigue behaviour for asphalt binders.

A new extensional test that measures the elongational rheological parameter referred to as extensional viscosity is introduced in this paper. It gives an indication of a material's resistance to extensional deformation (i.e. elongation induced by stretching). It determines the behaviour of a thin film of bitumen as it occurs *in-situ* within the asphalt pavement or seal layer. An extensional test method that requires very small sample sizes for testing is important when insufficient binder is available for testing, as typically expected for recovered bitumen from field asphalt or seal samples.

II. BACKGROUND

There are three types of extensional deformation, namely uniaxial, biaxial and planar [8]. According to Baird [8], uniaxial extension, the simplest form of extensional deformation, is the popular extensional characterisation technique for visco-elastic materials. In uniaxial extension, the stretching of a substance in one direction leads to contraction of the substance in the other two directions; and elongation in the direction of stretching [9].

The resistance presented by a substance to this kind of deformation is called uniaxial extensional viscosity ($\eta_E{}^+$), which is given by (1) as the ratio of extensional stress (σ_E) to extensional rate (Hencky strain rate) ($\dot{\varepsilon}_H$) [9]. See Fig. 1a for the operational principle of extensional viscosity measurements.

$$\eta_E{}^+ = {}^{\sigma_E}/_{\dot{\varepsilon}_H} \qquad (1)$$

Extensional stress is also called tension. It is given by (2) below; where F and A are the force and area.

$$\sigma_E = {}^{F}/_{A} \tag{2}$$

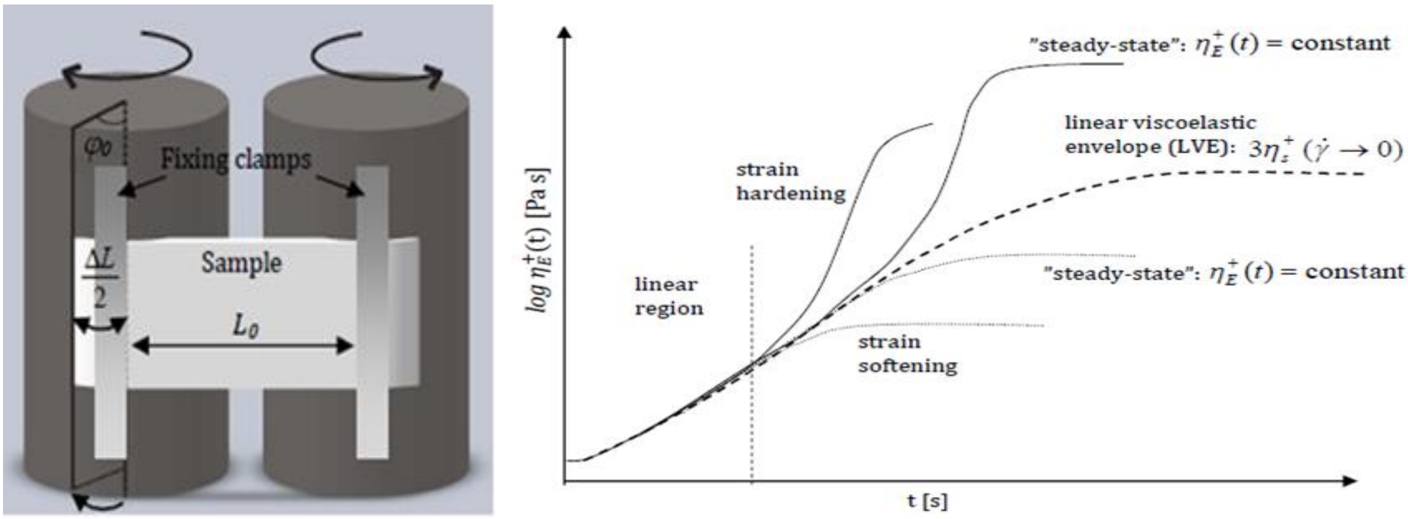
Extensional rate (Hencky strain rate) is the rate at which the material is stretched. It is defined by (3) below; where Ω is constant drum rotating speed, R is the drum radius and L_0 is the initial length of the sample being stretched.

$$\dot{\varepsilon}_H = {}^{2\Omega R}/_{L_0} \tag{3}$$

Extensional viscosity has been used to characterise polymer melts but it is scarcely used to characterise bitumen.

The Trouton ratio relates extensional and shear properties [10]. In ideally viscous flows, the corresponding shear viscosity is a third of uniaxial extensional viscosity [10]. However, there is a deviation from this rule in visco-elastic behaviour-where extensional viscosity increases with time before reaching steady state for strain hardening materials [10]. Strain hardening is common in branched or partially cross-linked polymers [11]. For strain softening materials, departure from Trouton's ratio is indicated by a steady state level that is below the linear viscoelastic envelope [10]. The concept of strain hardening and strain softening is summarised in Fig. 1b. It is this sensitivity of these flows to molecular structure at certain strain envelopes that make this technique ideal for fingerprinting bitumen, especially when modified by polymers.

Petrie's [12] debate on the use of the term, transient extensional viscosity, is noted. In this study though, the aim is to use the term in classification and categorisation only, for flows that are not steady or spatially uniform [12].



(a) (b)

Fig. 1. (a) Operational principle of extensional viscosity measurements, (b) Transient uniaxial extensional flow [10].

III. EXPERIMENTAL

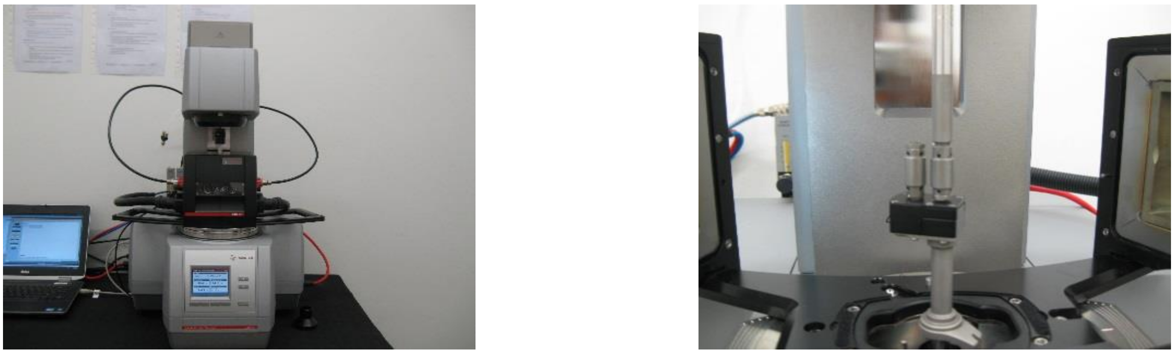
A. *Equipment*

Rheometers are commonly used instruments to measure extensional viscosity. They have developed substantially from the initial home built extensional rheometers [13,14,15]. The introduction of fixed rotating fixtures to replace moving clamps [16] have allowed the total extension to be unlimited by the apparatus size [17].

For this study, measurements were carried out with the MCR 502 TwinDrive Dynamic Shear Rheometer with a CTD 450 (Convection Temperature Device), using a Universal Extensional Fixture / TwinDrive (UXF/TD) measuring configuration (see Fig. 2 below). It uses a pair of counter rotating drums, eliminating errors emanating from the non-rotating end of the sample experienced in previous versions [18]. Measurements were done by both Anton Paar Germany and CSIR South Africa.

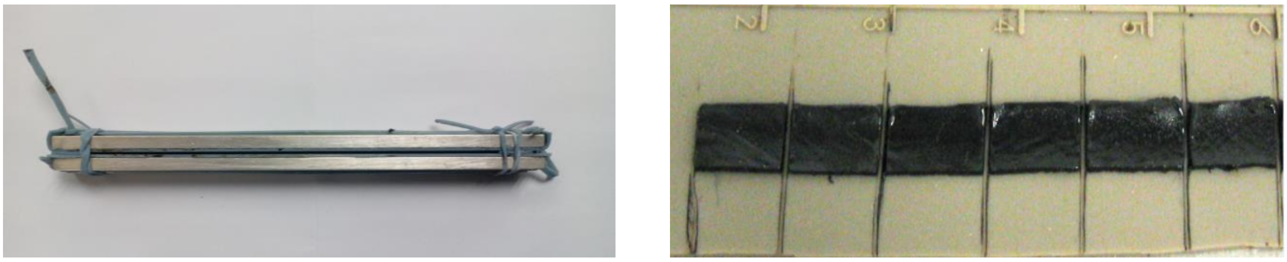
Measurements were carried out using bitumen films of 1±0.2mm thickness and 10mm width. Only 15g of bitumen was required to prepare a sample that produced ten test specimens. The thin films were produced in the set-up shown in Fig. 3a, using the bending beam rheometer (BBR) moulds that were slightly modified to produce thinner films. The bitumen films produced are shown in Fig. 3b.

A notable limitation of this study is that test results could not be compared to standard viscoelastic reference materials.



(a) (b)

Fig. 2. (a) MCR 502 TwinDrive with CTD 450, (b) UXF/TD fixture.



(a) (b)

Fig. 3. (a) Set-up for producing thin bituminous films, (b) Cut-outs of thin bituminous films.

B. *Samples*

The following unmodified binders were used in this investigation:

- 10/20 penetration grade bitumen
- 20/30 penetration grade bitumen
- 35/50 penetration grade bitumen
- 50/70 penetration grade bitumen
- 70/100 penetration grade bitumen

The following modified binders were used in this investigation:

- A-P1 (EVA modified bitumen)
- A-E1 (SBS modified bitumen-low polymer content)
- A-E2 (SBS modified bitumen-high polymer content)
- Wax modified bitumen
- Elvaloy (RET modified bitumen)

C. *Methodology*

After preparation, samples were initially stored at 16°C. Sample cutting and fixing onto the drums of the UXF measuring system were done with samples at 16°C to avoid sample stretching and altering their dimensions. The bitumen samples naturally stick between the drums of the UXF measuring geometry, making it unnecessary to use fixing clamps. It was imperative however, that the samples be prepared in length.

Process of sample cutting and fixing onto drums is a major influence on the measuring curve at the beginning of the test. For certain test results, a correction had to be made but only the corrected test curves are shown in this report. It was also noted that the sample thickness was not very uniform during measurement.

The determination of the transient extensional viscosity (η_E^+) of the bitumen film samples was carried out at room temperature (25°C).

Before starting the measurement, the software was set to counter-rotating mode, meaning that the drum which is connected to the upper motor turned counter-clockwise while the drum which was connected to the lower motor turned clockwise.

The measurement procedure consisted of two intervals. In the first interval, the sample was pre-stretched at a constant torque of 5μNm for 30 seconds. In the second interval, both drums rotated at a given strain rate until the total deflection angle of 450° was reached. Initially, testing was done at the strain rates of $0.001s^{-1}$, $0.01s^{-1}$, $0.1s^{-1}$ and $1s^{-1}$ (see pictures of the tested samples in Fig. 4 below), before a strain rate of $0.1s^{-1}$ was fixed.

An indication of the reproducibility of the test procedure at a strain rate of $0.1s^{-1}$ is shown in Table I, for 50/70 penetration grade binder films and SBS modified binder films. The coefficients of variation of the test appear to improve with extensional time.

Sample	Before Test	After setting a strain rate of 0.1 s^{-1}	After setting a strain rate of 1 s^{-1}
Modified Binder			
Unmodified Binder			

Fig. 4. Pictures of bitumen film samples before and after setting a strain rate.

TABLE I. COEFFICIENTS OF VARIATION OF THE TRANSIENT EXTENSIONAL PROPERTY AT DIFFERENT EXTENSIONAL TIME INTERVALS

BINDER	**Extensional Time Interval**		
	5s	**15s**	**25s**
50/70pen grade binder	9.2 %	4.6 %	2.9 %
SBS modified binder	9.9 %	7.5 %	6.1 %

IV. RESULTS

A. *Unmodified binders*

Transient extensional viscosity curves for unmodified binder films are shown in Fig. 5 and 6. After the initial linear region, these binders exhibit a levelling out of transient extensional viscosities once they reach a plateau (Fig. 5), which tends to be higher the stiffer the binder. This behaviour is similar to that of uncross-linked polymers [19], and this finding supports the conclusion of previous studies [20]. Beyond the steady-state behaviour, the transient extensional viscosities eventually decrease. The lower the strain rate, the longer the extensional time interval prior to the onset of this decrease (see Fig. 6), possibly suggesting "necking" behaviour [19].

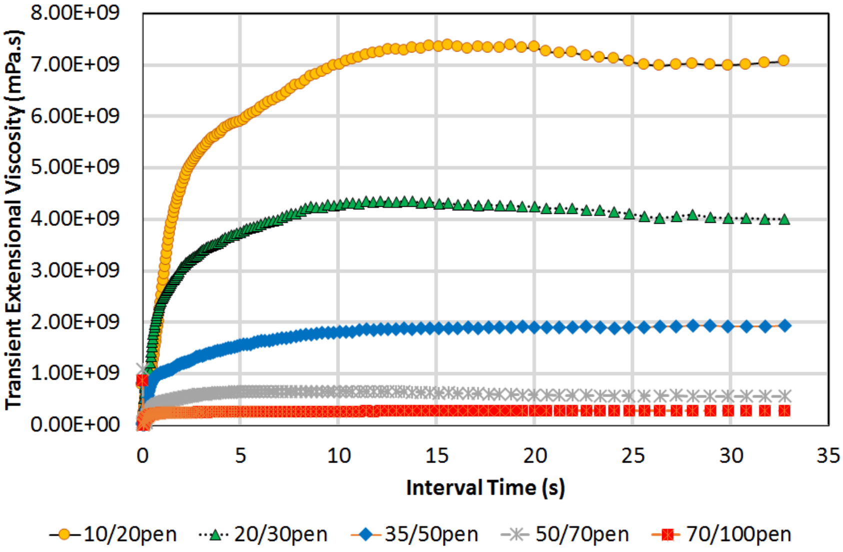


Fig. 5. Transient extensional viscosity of various unmodified bitumen film samples at a strain rate of $0.1s^{-1}$.

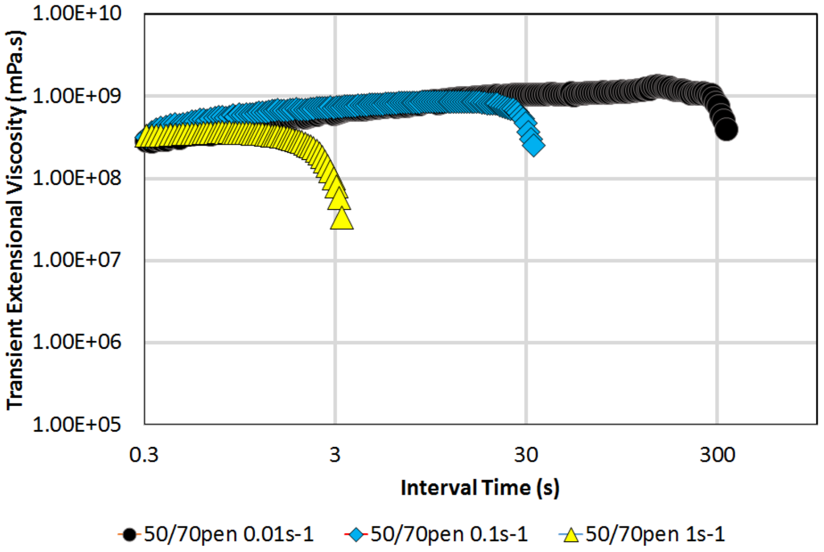


Fig. 6. Transient extensional viscosity of 50/70pen grade bitumen film samples at different strain rates.

B. *Modified binders*

Fig. 7 and 8 show a strain hardening effect of an SBS modified binder when compared to an unmodified binder and occurring at various strain rates, respectively. This means the resistance to extensional deformation increases as the SBS modified binder film is pulled apart. This behaviour is typical for branched or partially cross-linked polymers [19], and this finding supports the conclusion of previous studies [20].

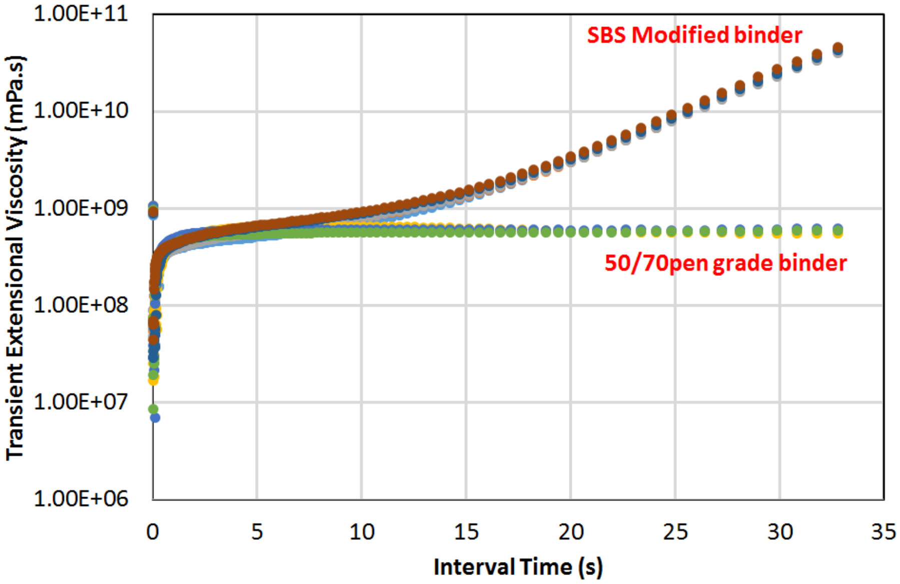


Fig. 7. Multiple transient extensional viscosity curves for a 50/70pen grade bitumen film samples and SBS modified bitumen film samples, at a strain rate of $0.1s^{-1}$.

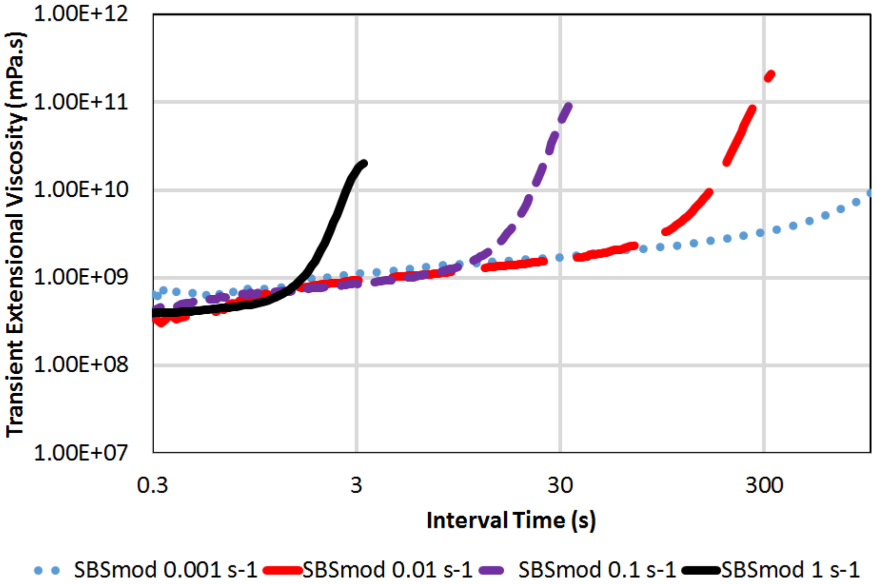


Fig. 8. Transient extensional viscosity of SBS modified bitumen film samples at different strain rates.

Fig. 9 shows the transient extensional viscosities of various modified bitumen films at $0.1s^{-1}$ strain rate. A strain hardening effect can be observed for four of the modified binders. The occurrence of this strain hardening is likely the result of a broad molar mass distribution and long chain branches that are found in the polymer modifiers. This effect distinguishes polymer modified binders from unmodified ones. However, the wax modified binder does not show this effect because wax is a regular chain material with very few/small branching points.

The figure also shows a clear difference in behaviour between bitumen modified with elastomers (SBS modified binders) compared to the plastomer, EVA modified bitumen (A-P1). The Elvaloy-RET modified bitumen showed transient extensional viscosities somewhere in-between, possibly suggesting mixed chemistry.

The higher SBS polymer content in A-E2 binders, as compared to A-E1 binders, is clearly noted in the strain hardening behaviour at higher transient extensional time intervals. Similarities of the SBS modified binders in their transient extensional viscosities at lower extensional time intervals imply that they are based on base binders of similar stiffness. For the plastomer (A-P1) and the wax modifier, their effect on bitumen seem more pronounced at earlier extensional time intervals.

The effect of different modifiers on the transient extensional viscosity parameter is somewhat similar to that observed with force ductility curves when monitoring the effect of modifiers on the primary and secondary peaks, see Fig. 10.

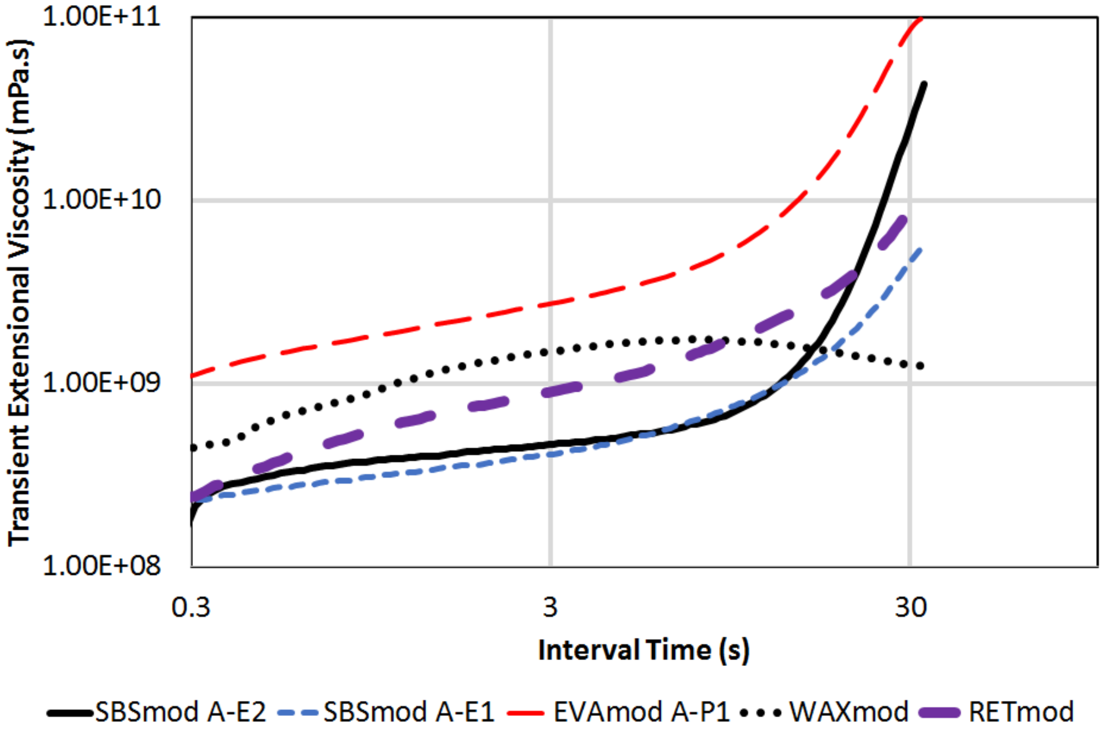


Fig. 9. Transient extensional viscosity of various modified bitumen film samples at a strain rate of $0.1s^{-1}$.

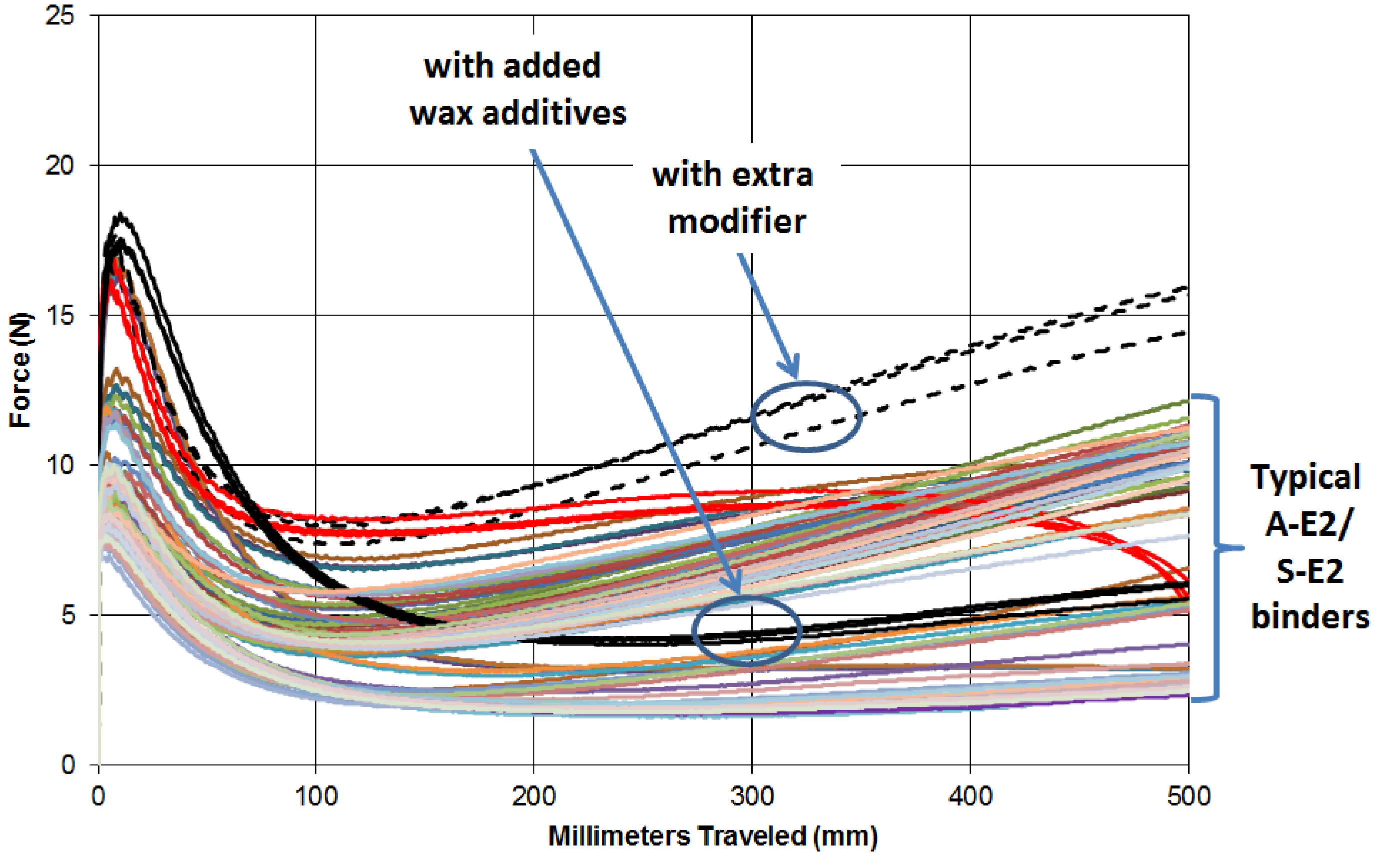
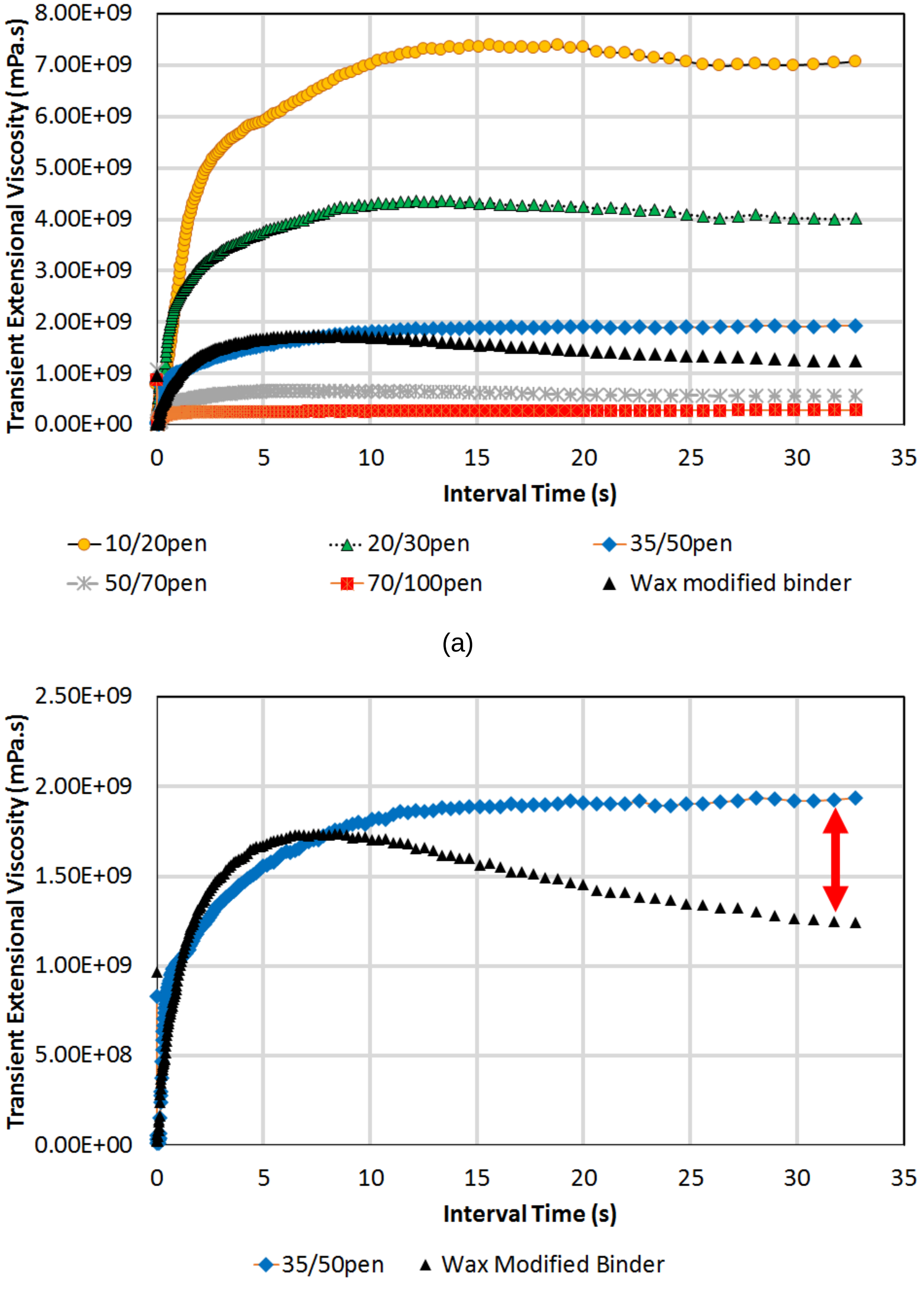


Fig. 10. Force-ductility curves of S-E2 and A-E2 modified binders at 15°C [4].

C. *Wax modified binders*

The wax modified binder, like the unmodified binders, did not exhibit any strain hardening effect. A distinction of such binders from unmodified binders is possible, although not clearly distinct. The wax modified binder is a blend of 50/70pen grade binder with 5% wax. The modification with wax has increased the transient extensional viscosities by a grade, to the level of the 35/50pen grade binder (see Fig. 11). However, the presence of wax has also modified the extensional curve of the binder. Once a plateau is reached, the steady-state interval is relatively shorter before the transient extensional viscosities gradually start to decline.

Given the stress sensitivity behaviour of wax modified bitumen observed in previous studies (see Fig. 12 [21]), it is recommended that this “softening” of these binders or their sensitivity at higher extensions warrants a further investigation to the stress and strain resilience and their implications during wax modification of bitumen.



(a)

(b)

Fig. 11. Transient extensional viscosity of wax modified bitumen film samples in comparison to unmodified bitumen film samples at a strain rate of $0.1s^{-1}$.

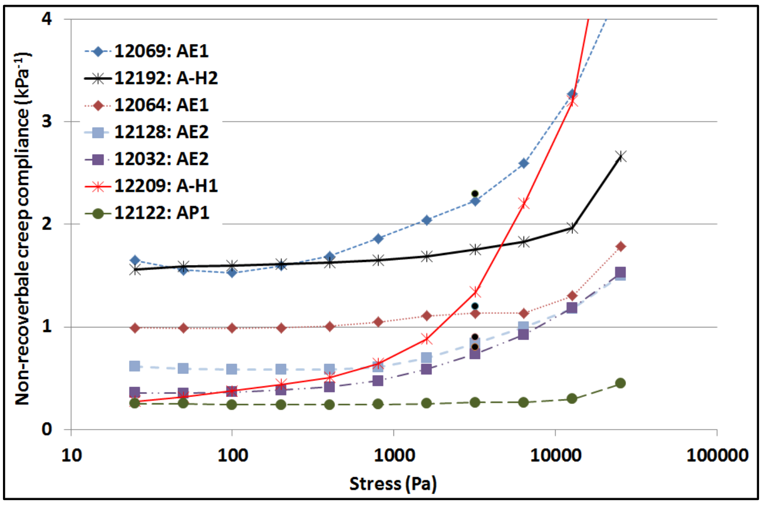


Fig. 12. Stress dependency of J_{nr} for modified binders at 64 °C, where A-H1 is a wax modified bitumen [21].

D. *Performance indication*

Maluke *et al*. [7] have reported on the success of the DENT test in fatigue prediction of binders in asphalt specimens tested with the four point bending beam device. So the behaviour of a test specimen with an induced dent (to create a weak point) at its centre was also investigated (see Fig. 13). The specimen broke towards the end of the measurement, and the data was converted to rheometric functions of extensional stress and displacement to create the curve shown in Fig. 14 that could potentially be used for calculating the work of fracture. This was a preliminary check, future work to specify the exact notch sizes and assess measurement errors as a result of specimen dimensional changes during measurement.

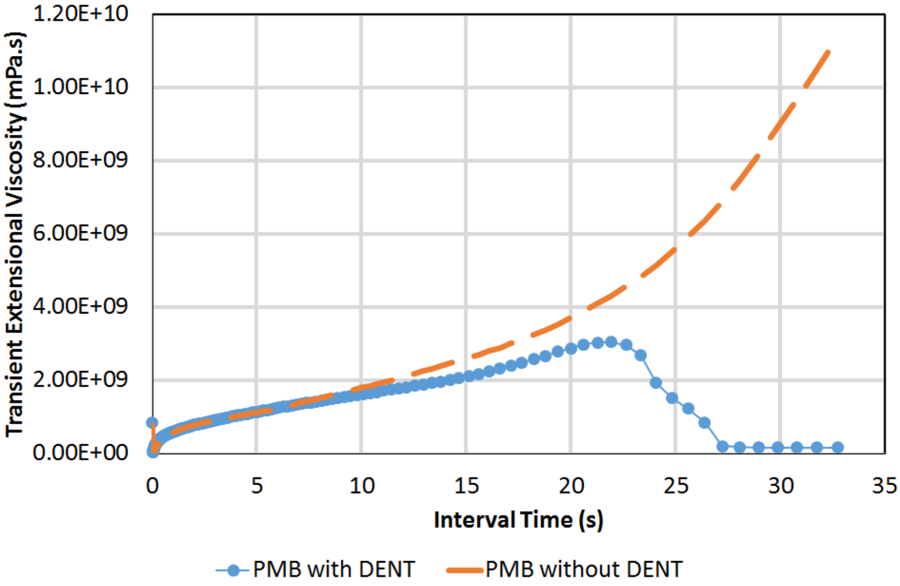


Fig. 13. Transient extensional viscosity of Elvaloy RET modified bitumen film sample at a strain rate of $0.1s^{-1}$.

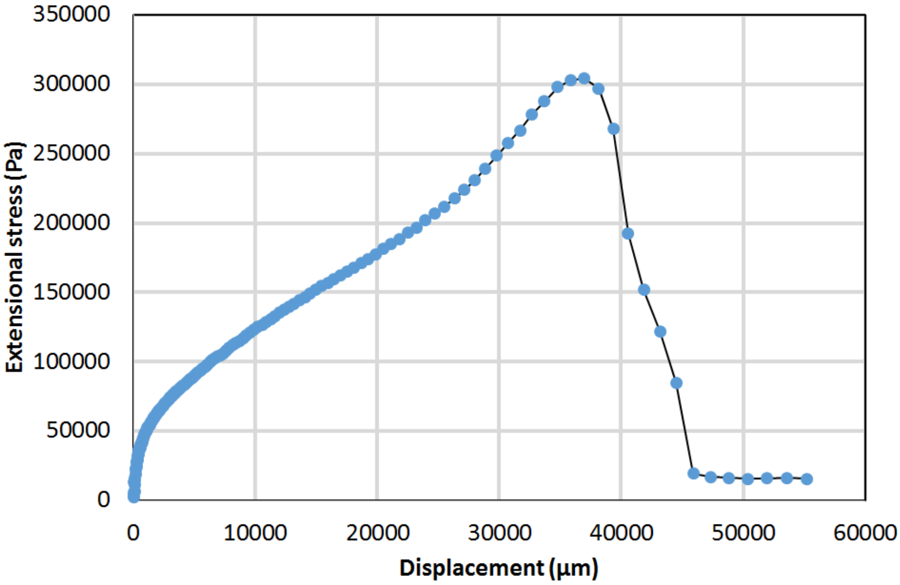


Fig. 14. Extensional stress vs. displacement of dented Elvaloy RET modified bitumen film sample at a strain rate of $0.1s^{-1}$.

I. CONCLUSION

The test method is able to distinguish between unmodified and modified bituminous binders based on their transient extensional viscosity at a constant strain rate. It can also provide key insights into the mechanism of action for these modifiers in bituminous materials.

For accurate measurements, test results will need to be compared to a standard viscoelastic reference material. Thereafter, further research should focus on characterising the effect of ageing of different bituminous binders in South Africa.

REFERENCES

[1] ASTM D113-17, Standard Test Method for Ductility of Asphalt Materials. West Conshohocken, PA: ASTM International, 2017.

[2] Technical Guideline 1 (TG1), The use of Modified Bituminous Binders in Road Construction, 2nd ed., Pretoria, Gauteng: Asphalt Academy, 2007.

[3] J. O'Connell, G. Mturi, J. Komba, and L. Du Plessis, "Analysis of the binder yield energy tests as an indicator of fatigue behaviour of asphalt mixes," Conference Proceedings of BESTInfra, Czech Technical University, Czech Republic, pp. 1-8, September 2017.

[4] G. Mturi and M. Nkgapele, "Force ductility – A 5 year feedback of performance results," 32nd Southern African Transport Conference, Pretoria, South Africa, July 2013.

[5] P.S. Kandhal, ASTM STP 628: Low temperature properties of bituminous materials and compacted bituminous paving mixtures (Marek, C.R., ed.): Low-temperature ductility in relation to pavement performance, Philadelphia, PA: American Society for Testing and Materials, pp 95-106, 1977.

[6] C.J. Glover, R.R. Davison, C.H. Domke, Y. Ruan, P. Juristyarini, D.B. Knorr, and S.H. Jung, Report No. FHWA/TX-05/1872-2: Development of a new method for assessing asphalt binder durability with field validation. Austin, Texas: Texas Transport Institute, College Station, Texas / Texas Department of Transportation, 2005.

[7] N. Maluke, G. Mturi, and S.A.M. Hesp, "Correlation of extensional bitumen properties with 4-point bending beam asphalt mixture fatigue life," 2018 SARF/IRF/PIARC, Durban, South Africa, October 2018.

[8] D.G. Baird, "The role of extensional rheology in polymer processing," Korea-Aust Rheol J., vol. 11, no. 4, pp. 305-311, 1999.

[9] H.A. Barnes, A Handbook of Elementary Rheology. Wales: The University of Wales Institute of Non-Newtonian Fluid Mechanics, 2000.

[10] J. Aho, PhD: Rheological characterization of polymer melts in shear and extension: measurement reliability and data for practical processing. Tampere: University of Tampere, 2011.

[11] F. Snijkers, R. Pasquino, P.D. Olmsted, and D. Vlassopoulos, "Perspectives on the viscoelasticity and flow behavior of entangled linear and branched polymers," J. Phys.: Condens. Matter, vol. 27 no. 47, pp. 1-13, 2015.

[12] C.J.S. Petrie, "Extensional viscosity: a critical discussion," J Nonnewton Fluid Mech, vol. 137, issues 1-3, pp. 15-23, 2006.

[13] H.J. Karam, K.S. Hyun, and J.C. Bellinger, "Rheological properties of molten polymers," Trans. Soc. Rheol., vol. 13, pp. 209-229, 1969.

[14] R.L. Ballman, “Extensional flow of polystyrene melt,” Rheologica Acta, vol. 4, pp. 137-140, 1965.

[15] F.N. Cogswell, “Tensile deformations in molten polymers,” Rheologica Acta, vol. 2, pp. 187-194, 1969

[16] J. Meissner, “Rheometer zur Untersuchung der deformationsmechanischen Eigenschaften von Kunststoff-Schmelzen unter definierter Zugbeanspruchung,” Rheologica Acta, vol. 8, pp. 78-88, 1968.

[17] P. Hodder and A. Franck, “A new tool for measuring extensional viscosity,” Annual Transactions - The Nordic Rheology Society, vol. 13, 2005.

[18] M. Sentmanat, B.N. Wang, and G.H. McKinley, “Measuring the transient extensional rheology of polyethylene melts using the SER universal testing latform,” J. Rheol., vol. 49, issue 3, pp. 585-606, 2005.

[19] T.G. Mezger, The Rheology Handbook, 4th ed., Hanover: Vincentz Network, 2014.

[20] G. Mturi, S. Zoorob, and J. O’Connell, “Effect of shear rate on bitumen viscosity measurements – relevance to high temperature processing of bituminous products,” 10th CAPSA, KwaZulu-Natal, South Africa: Champagne Sports Resorts, 2011.

[21] J. O'Connell, G. Mturi, and S.Zoorob, " A review of the development of the non-recoverable compliance, Jnr, for use in South Africa,” 11th CAPSA, Sun City, South Africa, August 2015.