MODELLING THE RHEOLOGICAL PROPERTIES OF BITUMINOUS BINDERS USING A MECHANICAL MODEL

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ABSTRACT

Modelling is a very useful way to fit or describe the linear viscoelastic (LVE) properties of bituminous binders, which cannot be done via laboratory work. This study investigates the applicability of LVE rheological models called the 2S2P1D (combinations of two springs, two parabolic elements and one dashpot) model on different types of bituminous binders. The rheological data of unaged and aged unmodified bitumens, bitumen-filler mastics and polymer-modified bitumens were measured using a dynamic shear rheometer (DSR) in the LVE region. It was found that this model with seven parameters fits the measurements reasonably well over a wide range of temperatures and frequencies. The correlation between measured and descriptive data was evaluated by means of the goodness-of-fit statistics method. Except for the unaged polymer-modified bitumens, the other samples show good agreement between the measured and descriptive complex modulus and phase angle data.

Keywords: *Bitumen-filler mastic, Linear viscoelastic, Modelling, Polymer modified bitumen, Unmodified bitumen*

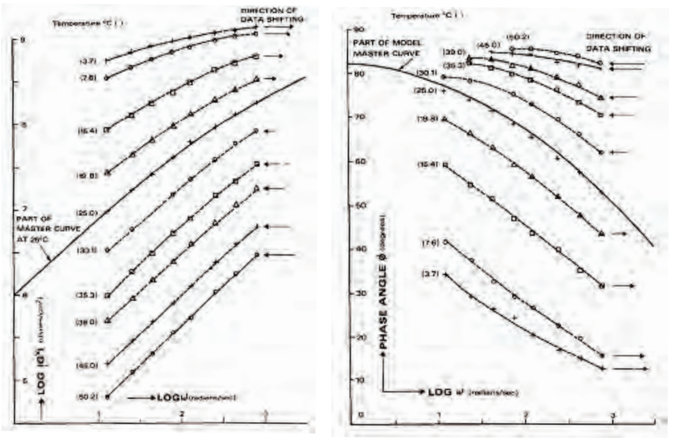
1.0 BACKGROUND

Traditionally, the behaviour of unmodified bitumen is evaluated using empirically based tests as part of penetration or viscosity graded specifications. The primary purpose of these specifications is to grade the unmodified bitumen according to its consistency and, therefore, they do not address specific distress modes or ensure good long-term field performance. With the increased use of bitumen modifications such as polymers and mastics, there is a need for fundamental binder testing, where the classical tests have proved inadequate, to describe the viscoelastic properties needed for a complete rheological evaluation of bitumens [1]. One such fundamental test is a dynamic shear rheometer (DSR), which was introduced during the Strategic Highway Research Program (SHRP) campaign. The DSR is a very useful tool to determine the elastic, viscoelastic and viscous properties of bituminous binders over a wide range of temperatures and frequencies [2]. This instrument, however, has a limitation: at high frequencies and/or low temperatures, data are exposed to testing errors from the rheometer [3-5]. Moreover, it is time-consuming, expensive and requires operation by skilled personnel if complete linear viscoelastic (LVE) properties are to be obtained.

Alternatively, the introduction of modelling is very useful to fit or describe the rheological properties of bitumen which cannot be obtained through experimental work. In general, there are several methods used to represent the rheological properties of binders: nomograph, mathematical equation and mechanical model. Historically, the development of the rheological models is dated circa 1950s when the Van der Poel's nomograph was introduced [1]. However, nomographs become obsolete with time and tended to be replaced with mathematical and mechanical models. In the mathematical equation approach, one simply has to adjusts any mathematical formulation whatsoever to the experimental main curve, with the quality adjustment being the sole criterion of choice of formulation. Meanwhile, in the mechanical element approach, use is made of the fact that the behaviour of LVE material can be represented by a combination of spring and dashpot mechanical models, resulting in a particular mathematical equation [6]. A number of studies have been conducted to develop rheological models, and all of them are generally able to satisfactorily describe the rheological properties of unmodified bitumen in the LVE region.

Normally, the dynamic shear data are presented as complex modulus $|G^*|$ and phase angle δ master curves, as shown in Figure 1 [7]. A good master curve should appear smooth and continuous. The technique of determining the master curve is based on the time-temperature superposition principle (TTSP) correspondence, which uses the equivalence between frequencies and temperatures to determine the moduli of bitumens. This principle involves the horizontal movement [8]. A standard reference temperature (T_{ref}) needs to be selected and the rheological data at all other temperatures shifted with respect to frequency until the lines merge into a single form. The amount of shifting required at each temperature to form the master curve is called the shift factor a_T. Materials whose rheological properties can be shifted by TTSP to produce a smooth, continuous master curve are termed thermo-rheologically simple materials [9].

According to Chailleux *et al.* [10], the construction of master curves only makes sense if there are no major structural rearrangements such as phase changes, and tests are conducted within the LVE response. Through the use of the master curve and shift factor relationships, it is possible to interpolate stiffness at an expanded range of frequencies and temperatures compared with those at which the data was collected. If functional forms are fitted to the shape of the master curve plot and to the shift factor relationship this interpolation becomes rapid and easy to apply in computer software. In addition, if a functional form with some thermodynamic basis is used then the resulting equations can be employed to extrapolate the data beyond the observed range of temperatures and frequencies [11].



(a) *(b)*

Figure 1: The construction of the (a) |G*| and (b) δ master curves [7]

From the literature, the 2S2P1D model was found to be a unique rheological model that is capable of fitting or describing the rheological properties of both the binder and asphalt mixture. This model was originally calibrated at the *Ecole Nationale des Travaux Publics de l'Etat* (ENTPE) laboratory using annular shear rheometer (ASR) data [12]. However, the validity of this model also needs to be assessed by other types of rheometers. Therefore, the objective of this study is to evaluate the suitability of the 2S2P1D model to describe the rheological properties of various binders from the dynamic shear rheometer (DSR) tests. The correlation between the measured and descriptive data is evaluated using the goodness-of-fit statistics method for both $|G^*|$ and δ master curves.

2.0 THE 2S2P1D MODEL

The 2S2P1D, an abbreviation of the combinations of two springs, two parabolic creep elements and one dashpot, is a unique model to fit or describe the rheological properties of binders and asphalt mixtures in the LVE region [12-14]. This model, as shown in Figure 2, is based on the generalisation of the Huet-Sayegh model (combinations of two springs and two parabolic elements in series).

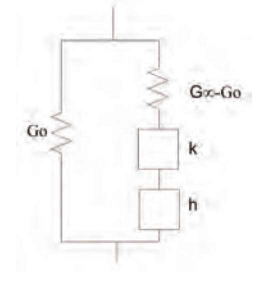


Figure 2: The 2S2P1D model [12]

According to Olard and Di Benedetto [12], a parabolic element is an analogical model with a parabolic creep function, and is shown as the following:

$$J(t) = a\left(\frac{t}{\tau}\right)^h \tag{1}$$

The complex modulus function is given by:

$$G^* = \frac{(\mathrm{i}\omega\tau)^h}{a\Gamma(h+1)} \tag{2}$$

where $J(t)$ is the creep function, h is the exponent where $0 < h < 1$, a is a dimensionless constant, t is the loading time, τ is the characteristic time (which value varies only with temperature), i is the complex number $\left(i = \sqrt{-1}\right)$ and ω is the angular frequency. Γ is a gamma function and defined as:

$$\Gamma(n) = \int_0^\infty t^{n-1}\, \mathrm{e}^t\, dt \tag{3}$$

where n is the number of points. The 2S2P1D model consists of seven parameters (G_∞, G_o, α, k, h, β and τ_o) and the complex modulus equation is shown as follows:

$$G^* = G_0 + \frac{G_\infty - G_0}{1 + \alpha(\mathrm{i}\omega\tau)^{-k} + (\mathrm{i}\omega\tau)^{-h} + (\mathrm{i}\omega\beta\tau)^{-1}} \tag{4}$$

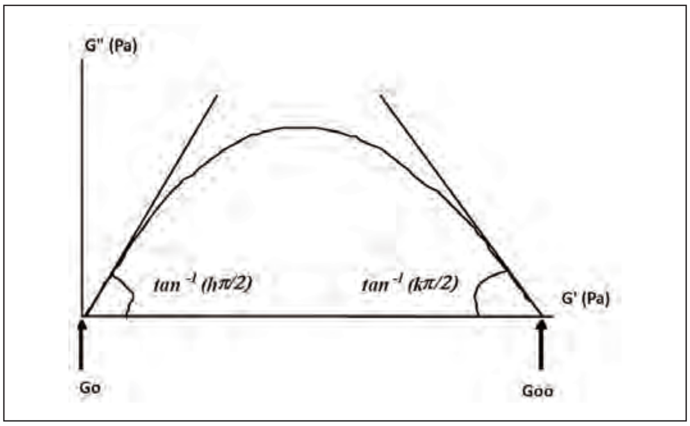
where k and h are the exponents with $0 < k < h < 1$, α is a parameter, G_o is the static modulus when $\omega \rightarrow 0$, G_∞ is the glassy modulus when $\omega \rightarrow \infty$. Meanwhile, β is a parameter and obtained from:

$$\eta = (G_\infty - G_0) \times \beta \times \tau \tag{5}$$

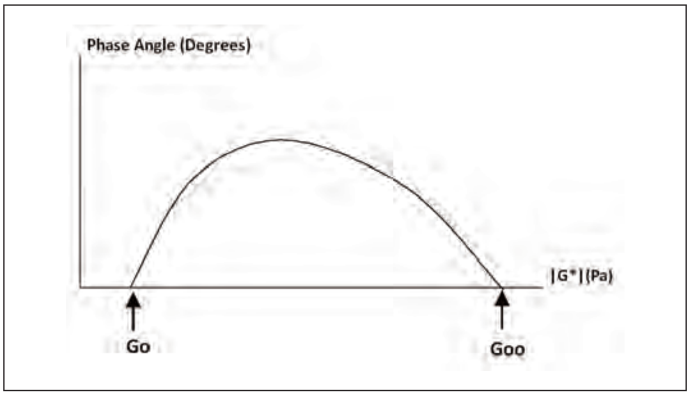
where η is the Newtonian viscosity and τ is a characteristic time that is only dependent of temperature and takes into account TTSP. The evolution of τ can be approximated by a shift factor law such as shifting the curve manually, the William, Landel and Ferry (WLF) equation and Arrhenius equation in the range of temperatures observed in the laboratory [12-14]:

$$\tau = a_T(T) \times \tau_0 \tag{6}$$

where $a_T(T)$ is the shift factor at temperature T_i, and τ_o is determined at the reference temperature T_{ref}. The 2S2P1D model only needs seven parameters to determine the entire rheological properties of materials [12]. The parameters (G_o, G_∞, k, h, and β) are determined iteratively to achieve the best fit that can be obtained in the Cole-Cole diagram and Black diagram respectively (Figures 3 and 4) [15]. By definition, the Cole-Cole diagram is a graph of the loss modulus G'' as a function of the storage modulus G' and the Black diagram is a graph of $|G^*|$ versus δ [6].



(a) The Cole-Cole diagram



(b) The Black diagram

Figure 3: Graphical representation of the model's parameters in term of (a) the Cole-Cole diagram and (b) the Black diagram [15]

Meanwhile, the phase angle δ is determined using the classical equation, shown as follows:

$$\delta = \tan^{-1}\left(\frac{G''}{G'}\right) \tag{7}$$

where the symbols are as previously defined. All the parameters are adjusted to ensure that the model's curve is superposed with measurements. This process is manually.

3.0 GOODNESS-OF-FIT

Three statistical methods are used to indicate the goodness-of-fit between measured and descriptive results [16]. The implementation of goodness-of-fit statistics is done using the MATLAB program.

3.1 The Discrepancy Ratio (r_i)

$$r_i = \frac{|G^*|_p}{|G^*|_m} \tag{8}$$

where $|G^*|_p$ and $|G^*|_m$ are the descriptive and measured complex modulus, respectively. The subscript i denotes the dataset number. For a perfect fit, $r_i = 1$.

3.2 The Mean Normalized Error (MNE)

$$\mathrm{MNE} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{|G^*|_m - |G^*|_p}{|G^*|_p}\right| \tag{9}$$

where N is the total number of datasets and for a perfect fit, $MNE = 0$.

3.3 The Average Geometric Deviation (*AGD*)

$$\mathrm{AGD} = \left(\prod_{i=1}^{N}\tilde{R}_i\right), \quad R_i = \begin{cases} |G^*|_p / |G^*|_m & \text{for } |G^*|_p \geq |G^*|_m \\ |G^*|_m / |G^*|_p & \text{for } |G^*|_p < |G^*|_m \end{cases} \tag{10}$$

where $AGD = 1$ for a perfect fit.

4.0 EXPERIMENTAL PROGRAMS

4.1 Materials

Various types of materials from the conducted experiments and the Nottingham Transportation Engineering Centre (NTEC) DSR database were used in this study. These include unaged and aged unmodified bitumens, polymer-modified bitumens (PMBs) and bitumen-filler mastics. 70/100 penetration grade bitumens were mixed with a plastomeric ethylene-vinyl acetate (EVA) polymer and an elastomeric styrene butadiene styrene (SBS) polymer to produce various polymer-modified bitumens. Three polymer contents (by mass) at 3, 5 and 7% were used to create several combinations of the EVA- and SBS- polymer-modified bitumens. Finally three different fillers namely gritstone, limestone and cement were mixed with 50 penetration grade bitumen at 40% (by weight) to produce various bitumen-filler mastics.

4.2 Dynamic Mechanical Analysis

The rheological properties of various materials were determined using dynamic mechanical methods consisting of temperature and frequency sweeps in an oscillatory-type testing mode performed within the LVE region. The oscillatory tests were conducted on a Bohlin Gemini dynamic shear rheometer (DSR) using two parallel plate testing geometries consisting of 8 mm diameter plates with a 2 mm testing gap and 25 mm diameter plates with a 1 mm testing gap (Figure 4). In this study, the samples were prepared using a hot pour method and a silicone mould method.

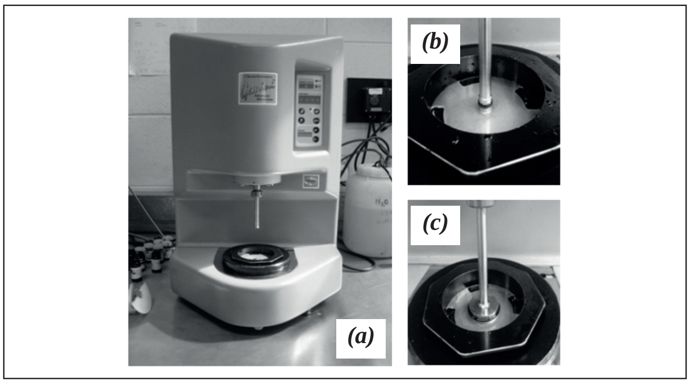


Figure 4: (a) The DSR body, (b) the 8 mm plates and (c) the 25 mm plates

In the hot pour method, the gap between the upper and lower plates was set to a desired height of 50 μm plus the required testing gap, either at the proposed testing temperature or at the mid-point of an expected testing temperature range. Once the gap has been set, a sufficient quantity of hot bitumen (typically between 100 – 150°C) was poured onto the lower plate of the DSR to ensure a slight excess of material appropriate to the chosen testing geometry. The upper plate of the DSR was then gradually lowered to the required nominal testing gap plus 50 μm. The bitumen that has been squeezed out between the plates was then trimmed flush to the edge of the plates using a hot spatula or blade. After trimming, the gap was closed by a further 50 μm to achieve the required testing gap as well as a slight bulge around the circumference of the testing geometry (periphery of the test specimen) [17].

Meanwhile, for the silicone mould method, the hot bitumen is poured into either an 8 mm or 25 mm diameter silicone mould of height approximately 1.5 times that of the recommended testing gap for the two geometries, namely 3 mm and 1.5 mm for the 8 mm and 25 mm geometries. The testing gap is set at a height of 50 μm plus 1 mm or 2 mm. Once the bitumen has cooled, either by means of short-term refrigeration or by natural cooling, the bitumen disc (typically at ambient temperatures) is removed from the mould and centred on the lower plate of the DSR. The upper plate is then lowered to the required gap plus 50 μm, the excess bitumen is trimmed with a hot spatula and the gap further closed to its final testing height [17].

Amplitude sweep tests are first conducted to determine the LVE region of the bituminous binders based on the point where $|G^*|$ has decreased to 95% of its initial value [18]. After obtaining the limiting strain, frequency sweep tests are carried out under the following test conditions:

Mode of loading	:	controlled-strain
Temperatures	:	10 to 80 °C (with the interval of 5 °C)
Frequencies	:	0.01 to 10 Hz
Spindle geometries	:	8 mm (diameter) and 2 mm gap (10 to 35 °C) and 25 mm (diameter) and 1 mm gap (25 to 80 °C)
Strain amplitude	:	within the LVE response, dependent on $|G^*|$ of each material used

For the construction of the $|G^*|$ and δ master curves, T_{ref} is arbitrarily taken at 10 °C. The curve is shifted manually, without assuming any shift factor forms.

4.3 Ageing Procedures

Short- and long-term laboratory ageing of the unmodified bitumens and polymer-modified bitumens were performed using the Rolling Thin Film Oven Test (RTFOT, ASTM D 2872) and the pressure ageing vessel (PAV, AASHTO PP1) respectively. The standard ageing procedures of 163 °C and 75 min for the RTFOT and 100 °C, 2.1 MPa and 20 h for the PAV were used. Meanwhile, the Thin Film Oven Test (TFOT, ASTM D1754) was used to age the bitumen-filler mastics at 1, 3, 5, 10 and 20 hours of ageing times. All the aged binders then subjected to DMA to evaluate changes in their rheological properties [18-19].

5.0 RESULTS AND DISCUSSION

5.1 Unaged Unmodified Bitumens

Table 1 shows the parameters (or constants) of the model used for simulation on different penetration grades of unaged unmodified bitumens. The materials tend to show Newtonian behaviour at high temperatures with G_o equal to zero, and therefore only six parameters of the model are needed to be determined. Interestingly, four of the model's parameters (G_∞, G_o, k and h) are found to be the same for all samples, regardless of the source of the crude and penetration grade bitumens. In this study, for simplification, G_∞ is taken as 1 GPa, as suggested for most engineering practical purposes [5]. Other parameters (α, β, τ, k and h) are determined iteratively to achieve the best fit based on the measured dynamic shear data.

Table 1: Parameters of the 2S2P1D model for unaged unmodified bitumens

Pen Grade	G_o (Pa)	G_∞ (GPa)	k	h	α	τ (x10^{-4})	β
10/20	0	1.00	0.22	0.64	5.00	60.00	90
35/50	0	1.00	0.22	0.64	4.00	15.00	75
40/60	0	1.00	0.22	0.64	3.50	3.00	90
70/100	0	1.00	0.22	0.64	3.00	0.50	90
160/220	0	1.00	0.22	0.64	2.30	0.35	45

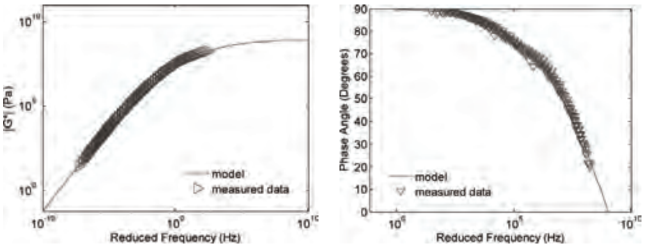
It is found that β for 10/20, 40/60 and 70/100 penetration grade bitumens is the same due to the fact that they have the same gradient at high temperatures. 160/220 penetration grade bitumen shows the lowest value of β. τ varies significantly for all materials, which shows that τ is time dependent. α decrease linearly from 10/20 penetration grade bitumen to 160/220 penetration grade bitumen. Di Benedetto and co-workers [12-13] show that α is approximately equal to 2.30 and consistent for all materials. It is believed that this phenomenon can be attributed to the fact that DSR data are affected by testing errors, particularly at high temperatures. Moreover, the different equipment used by the respective researchers may play a significant role in the data precision.

For a comparison between the measured and descriptive $|G^*|$ and δ master curves, the Cole-Cole diagram and the Black diagram are shown in Figure 5. For brevity, only 35/50 penetration grade bitumen is shown here with the understanding that the commentaries apply to all other conventional bitumens.

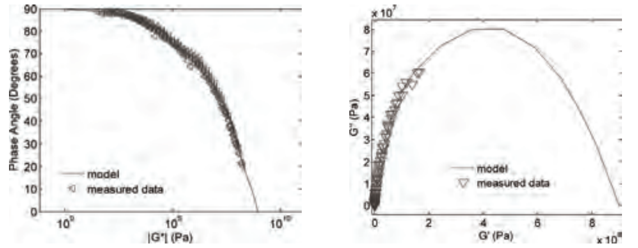
The 2S2P1D model is able to fit reasonably well with the measured $|G^*|$ and δ data. The Black and Cole-Cole diagrams show that the unaged unmodified bitumen data are consistent and can therefore be classified as the thermo-rheological simple materials. It is inferred that the 2S2P1D model is able to describe the rheological properties of unaged unmodified bitumens satisfactorily.

5.2 Unaged Bitumen-Filler Mastics

Mastics, composed of bitumen and filler, is an intermediate material between bitumen and asphalt mixture [19-20]. The presence of filler cannot therefore be neglected and have important effects such as improving the surface area, strength, plasticity, amount of voids, resistance to water action and



(a) The |G| master curve* *(b) The δ master curve*



(c) The Black diagram *(d) The Cole-Cole diagram*

Figure 5: A comparison between the measured and descriptive data of unaged unmodified bitumen

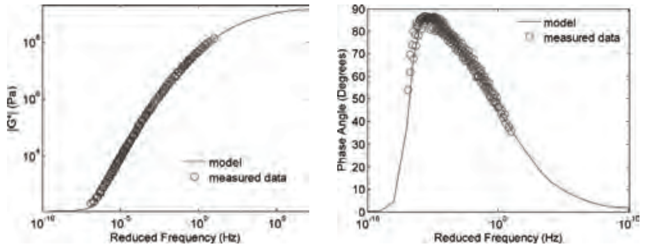
resistance to weathering [20]. Three different types of fillers– cement, gritsone and limestone– are used in this study, and the parameters of the model used for simulation for each bitumen-filler mastic are shown in Table 2. In general, *k, h* and β respectively, are the same for all fillers studied. This indicates that all samples have the same gradient at high temperatures.

Table 2: Parameters of the 2S2P1D model for bitumen-filler mastics

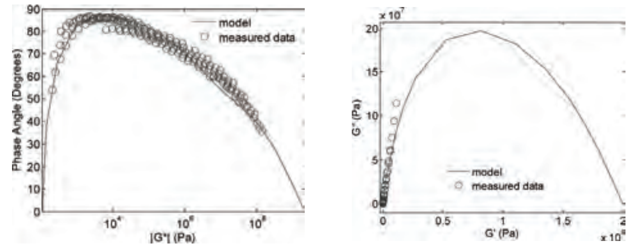
Material	G_o (Pa)	G_∞ (GPa)	k	h	α	τ (x10^{-4})	β
Gritstone	600	4.00	0.21	0.55	4.00	1.10	250
Limestone	10	2.00	0.21	0.55	4.00	4.00	250
Cement	120	2.00	0.21	0.55	4.00	3.00	250

The presence of filler mastics can be observed where G_∞ is higher than for the unaged unmodified bitumens and G_o should not be taken as zero. Delaporte *et al.* [13-14] report that this phenomenon can be attributed to the existence of solid contacts between particles. The results show that G_o for cement and gritstone bitumen-filler mastics are an order of magnitude greater of 1 and 2 respectively than the limestone bitumen-filler mastics. Among these fillers, limestone and cement are basic fillers, whereas gritstone is acidic, therefore the gritstone bitumen-filler mastic shows higher $|G^*|$ values at both higher and lower temperatures.

For a comparison between the measured and descriptive $|G^*|$ and δ master curves, the Cole-Cole and Black diagrams for unaged cement bitumen-filler mastic are shown in Figure 6. Like unaged unmodified bitumens, the 2S2P1D model shows a good correlation with the measured $|G^*|$ and δ data. At low frequencies, the δ master curve increases until it reaches the pinnacle point. δ decrease as the frequencies decreases and the filler shows a dominant role in the mixture's stiffness. The effects of fillers are shown where the measured data are slightly scattered in the Black and Cole-Cole diagrams. However, the 2S2P1D model is still able to satisfactorily describe the rheological properties of the bitumen-filler mastics.



(a) The |G| master curve* *(b) The δ master curve*



(c) The Black diagram *(d) The Cole-Cole diagram*

Figure 6: A comparison between the measured and descriptive data of unaged bitumen-filler mastics

5.3 Unaged Polymer-Modified Bitumens

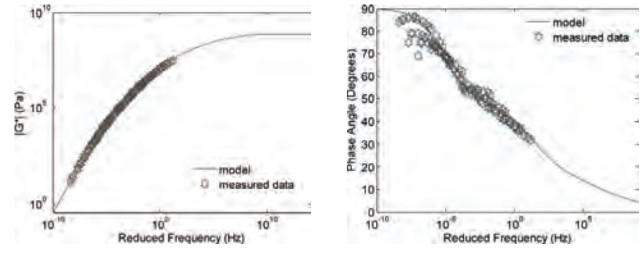
Table 3 shows the parameters of the model used for the simulation of unmodified (control sample) and polymer-modified bitumens. Two type of polymers– etylene-vinyl-acetate (EVA) and styrene-butadiene-styrene (SBS) – are mixed with the 70/100 penetration grade bitumen at different percentages. As suggested by Lu *et al.* [21], the value of G_∞ can be taken as 1 GPa for polymer-modified bitumens. The parameters (G_∞, G_o, *k* and *h*) are the same for one polymer-modified bitumen compared to the other, but α, τ and β vary. A similar observation has been made for the control sample. As shown in Table 3, α is inconsistent between the control sample and the EVA- and SBS-modified bitumens. This could be attributed to the fact that where data at high frequencies and/or low temperatures are exposed to testing errors. For bitumen modification, α is more consistent for the SBS-modified bitumen compared to the EVA-modified bitumen. This is probably due to the fact that the presence of the EVA semi-crystalline structure at different temperatures increases the complexity of the bitumens. A thorough discussion of the rheological properties of EVA- and SBS-modified bitumens can be found in previous publications [17-18, 22-24].

Table 3: Parameters of the 2S2P1D model for EVA and SBS-modified bitumens

Percent	Modifier	G_o (Pa)	G_∞ (GPa)	k	h	α	τ (x10^{-4})	β
0	Unmodified	0	1.00	0.21	0.55	3.50	0.50	150
3	EVA	0	1.00	0.21	0.55	3.50	0.50	600
5		0	1.00	0.21	0.55	3.00	0.60	1000
7		0	1.00	0.21	0.55	2.30	0.60	6000
3	SBS	0	1.00	0.21	0.55	2.30	0.30	1500
5		0	1.00	0.21	0.55	2.30	0.30	3000
7		0	1.00	0.21	0.55	2.30	0.50	20000

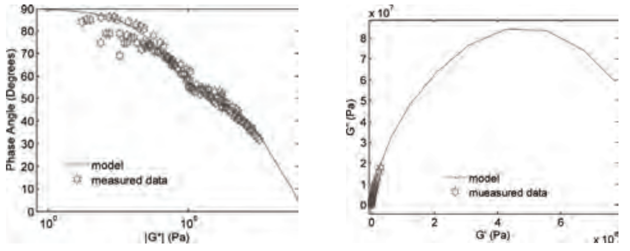
Meanwhile, β increases as the percentage of modifier is increased. The presence of polymer modification increases the viscosity of the mixtures. Figure 7 shows an example of $|G^*|$ and δ master curves, the Black and Cole-Cole diagrams for 7% EVA-modified bitumen. The 2S2P1D model shows a good correlation with the measured $|G^*|$. However, this model is unable to show a good fitting with the measured δ where data are dispersed particularly between 65 and 85^o. Similarly, the Black diagram shows that the model deviates from the measured data. The Cole-Cole diagram shows a good correlation between the measured and descriptive data. However, more data at low temperatures are needed for a better graphical representation in that diagram.

Olard and Di Benedetto [12] discovered an identical problem where a breakdown of the time-temperature superpostion principle (TTSP) above 10 ^{o}C is observed for polymer-modified bitumens. They classify this property as the partial time-temperature superposition principle (PTTSP), as the shifting procedure gives a continuous master curve only for $|G^*|$. The introduction of the PTTSP appears to be an alternative to the concept of thermo-rheologically complex (not thermo-rheological simple) behaviour of materials [12].



(a) The |G*| master curve

(b) The δ master curve



(c) The Black diagram

(d) The Cole-Cole diagram

Figure 7: A comparison between the measured and descriptive data of unaged polymer-modified bitumens

5.4 Aged Unmodified Bitumen

The existence of an important change in behaviour due to binder ageing has been observed mainly at higher temperatures and/or lower frequencies. Table 4 shows the parameters of the model used for simulation for unaged (control sample) and aged unmodified bitumens. The parameters (G_∞, G_o, k and h) are the same for the unaged and aged samples. β that links to the Newtonian viscosity η of the 2S2P1D model has a large influence at high temperatures [12]. Ageing mainly affects β. Ageing adsorbs the asphaltenes and renders the bitumens stiffer. The values of β increase from unaged to aged unmodified bitumens. This affects the dynamic shear data by an increase in $|G^*|$ data at high temperatures and decreases δ. Meanwhile α also increases from unaged to aged materials. Delaporte *et al.* [13] discovered the same finding, where α increases from 2.3 to 3.0 when comparing the $|G^*|$ master curves of unaged and aged unmodified 50/70 penetration grade bitumen. Therefore, α can be used as an "ageing indicator", where a higher value of α indicates that the materials are susceptible to ageing.

Table 4: Parameters of the 2S2P1D model for aged unmodified bitumen

Method*	G_o (Pa)	G_∞ (GPa)	k	h	α	τ (x10^{-4})	β
Unaged	0	1.00	0.21	0.55	3.50	0.50	150
RTFOT	0	1.00	0.21	0.55	5.00	0.50	400
PAV	0	1.00	0.21	0.55	5.00	4.00	1500

RTFOT: Rolling Film Thin Oven Test, PAV: Pressure Vessel Ageing

5.5 Aged Bitumen-Filler Mastics

An attempt has also has been made to model aged bitumen-filler mastics using the 2S2P1D model (Table 5). However, the cement bitumen-filler mastics data from Wu's study [19] are inconsistent and therefore the experimental results have been discarded.

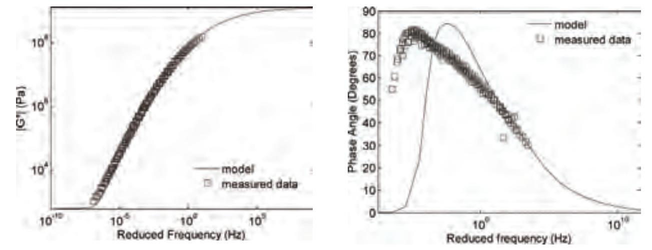
Table 5: The model parameters for aged bitumen-filler mastics

Material	Time (h)	G_o (Pa)	G_∞ (GPa)	k	h	α	τ (x10^{-4})	β
Gritstone	1	200	1.40	0.21	0.55	2.30	9.50	150
	3	12000	1.60	0.21	0.55	2.30	6.00	150
	5	8000	1.70	0.21	0.55	2.30	8.00	150
	10	600	1.40	0.21	0.55	2.30	20.00	150
	20	600	1.00	0.21	0.55	2.30	100.00	600
Limestone	1	8	1.50	0.21	0.55	2.30	5.50	150
	3	10	1.50	0.21	0.55	2.30	8.00	150
	5	10	1.50	0.21	0.55	2.30	10.00	150
	10	10	1.20	0.21	0.55	2.30	20.00	150
	20	3000	1.30	0.21	0.55	2.30	20.00	800

The gritstone and limestone bitumen-filler mastics yield the same values of parameters (k, h, δ and β) for ageing times from 1 to 10 hours. However, as the ageing time increases up to 20 hours, β increases up to 600 for gritstone bitumen-filler mastic and 800 for limestone bitumen-filler mastic respectively. Like unaged bitumen-filler mastics, G_o cannot be taken as zero due to the existence of solid contacts between particles. The acidic gritstone bitumen-filler mastic shows a big difference in G_∞ with ageing times compared to the limestone bitumen-filler mastic. In his work, Wu [19] shows that $|G^*|$ for gritstone bitumen-filler mastic increases as the ageing time increases. However, an initial reduction is observed for $|G^*|$ (at higher temperatures) of the limestone bitumen-filler mastic with the lowest value after one hour of ageing time. This phenomenon is believed to be caused by the adsorption of heavier fractions from bitumen to the mineral surface of the limestone bitumen-filler mastics [19].

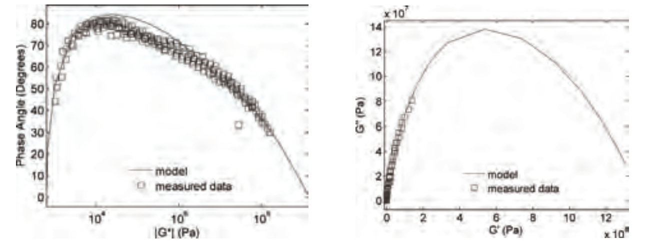
As an example of aged cement bitumen-filler mastics $|G^*|$ and δ master curves, the Black and Cole-Cole diagrams are shown in Figure 8. The 2S2P1D model correlates well with the measured $|G^*|$ but shows a poor correlation with the measured δ. A similar observation is made in the Black diagram, where this model shows a slight deviation from the measured δ between

70 and 85°. However, the Cole-Cole diagram shows a good correlation between the measured and descriptive data. The PTTSP principal can also be implemented on aged bitumen-filler mastics where the shifting procedure gives a continuous master curves only for $|G^*|$.



(a) The |G*| master curve

(b) The δ master curve



(c) The Black diagram

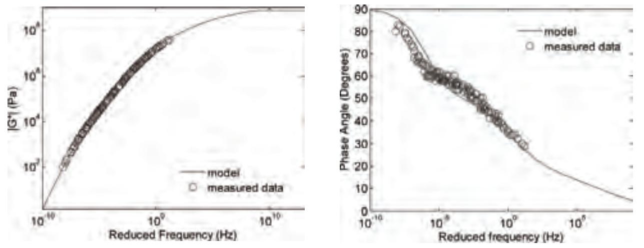
(d) The Cole-Cole diagram

Figure 8: A comparison between the measured and descriptive data of aged bitumen-filler mastics

5.6 Aged Polymer-Modified Bitumens

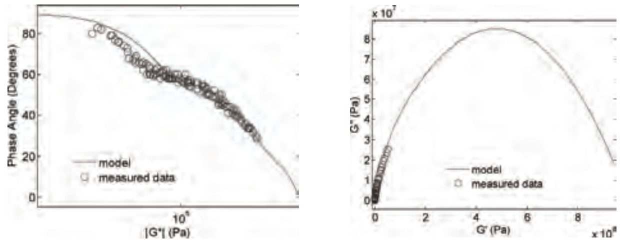
The parameters used for simulation on the aged polymer-modified bitumens are shown in Table 6. G_∞, G_o, k and h respectively are consistent between one material and the other. β increases as the percentage of modifications is elevated. However, for certain samples, the changes of α depend on the percentage of modifications used. It is believed that the values of α from RTFOT- to PAV-aged materials are affected by the hardness of the samples and also ageing itself.

Figure 9 shows an example of the $|G^*|$ and δ master curves, the Black diagram and Cole-Cole diagram for aged 7% SBS-modified bitumen. Airey [9] found that the effect of ageing can be seen as an alteration of the Black diagram "waves" associated with the different crystalline structures and a general reduction in polymer modification. Meanwhile, the effect of ageing on the polymer-dominant regions for SBS-modified bitumen relate to a shifting of the rheological properties towards a greater viscous response as a result of the thermo-oxidative degredation of SBS-modified bitumen [9]. Therefore, the PTTSP is implied for aged polymer-modified bitumens.



(a) The |G*| master curve

(b) The δ master curve



(c) The Black diagram

(d) The Cole-Cole diagram

Figure 9: A comparison between the measured and descriptive data of aged polymer-modified bitumens

5.7 Goodness-of-fit

Tables 7 and 8 show the goodness-of-fit statistics between the measured and descriptive data of $|G^*|$ and δ. The discrepancy ratio r_i is used to observe the descriptive data's tabulation from the equality line, with a perfect value equal to one. When the r_i is larger or smaller than one, it measures how much wider the prediction interval has to be to cover the observed number of cases. With the interval of ±4% used in this study, the unaged unmodified bitumen data are dispersed closely to the equality

Table 6: The model parameters for aged EVA and SBS-modified bitumens

Method	%	Modifier	G_o (Pa)	G_∞ (GPa)	k	h	α	τ ($\times 10^{-4}$)	β
RTFOT	3	EVA	0	1.00	0.21	0.55	4.50	1.00	1500
	5		0	1.00	0.21	0.55	5.00	3.00	2000
	7		0	1.00	0.21	0.55	5.00	2.00	10000
PAV	3		0	1.00	0.21	0.55	7.00	5.00	2500
	5		0	1.00	0.21	0.55	7.00	20.00	3000
	7		0	1.00	0.21	0.55	7.00	20.00	10000
RTFOT	3	SBS	0	1.00	0.21	0.55	4.00	0.30	1800
	5		0	1.00	0.21	0.55	5.00	0.15	8000
	7		0	1.00	0.21	0.55	5.00	0.30	8000
PAV	3		0	1.00	0.21	0.55	5.00	1.00	6000
	5		0	1.00	0.21	0.55	5.00	0.30	5000
	7		0	1.00	0.21	0.55	5.00	3.00	8000

RTFOT: Rolling Film Thin Oven Test, PAV: Pressure Vessel Ageing line, followed by aged unmodified bitumens, unaged bitumen-filler mastics, aged filler mastics and aged polymer-modified bitumens. As expected, the unaged polymer-modified bitumens show the least correlation between the measured and descriptive $|G^*|$ data.

Like r_i, the MNE and AGD are also used to observe the difference between the measured and descriptive data. The unaged unmodified bitumens show the most outstanding correlation, with MNE = 8.73 and AGD = 1.09 for $|G^*|$ and MNE = 1.79 and AGD = 1.02 for δ respectively, followed by the aged unmodified bitumens, unaged bitumen-filler mastics, aged polymer-modified bitumens, aged bitumen-filler mastics and unaged polymer-modified bitumens. The presence of high asphaltenes in aged bitumen-filler mastics and polymer-modified bitumens renders a breakdown in TTSP. The materials are classified as the thermo-rheological complex materials. Additionally, ageing might possibly affect the breakdown in polymer structure, therefore decreasing the effect of the polymer-rich phase network in the mixtures.

6.0 CONCLUSION

The following conclusions are drawn from this study:

i. The 2S2P1D model is quite simple in its formulation, as a combination of springs, dashpot and parabolic elements. The calibration of the model is not a very difficult tasks provide very good modelling for unmodified and modified bitumens over a wide range of frequencies and temperatures.

ii. It is observed that this model is able to fit the rheological properties of unmodified bitumens (unaged and aged), bitumen-filler mastics (unaged and aged) and polymer-modified bitumens (aged). However, the model failed to fit the rheological properties of unaged polymer-modified bitumens particularly with high modifications. The fit is even worse when a comparison is made for measured and descriptive δ.

iii. For modelling purposes, the G_g values can be taken as 1 X 10^9 Pa for unmodified and polymer-modified bitumens, both unaged and aged samples. They approach a limiting maximum modulus at very low temperatures.

iv. For the unaged and aged bitumen-filler mastics, the G_g values vary. The G_g values depend on the percentage and a type of mineral fillers used. This phenomenon occurs due to the existence of physical interaction in the mixture. ■

Table 7: Goodness-of-fit for complex modulus data

Sample	Condition	Discrepancy ratio, r_i					AGD	MNE
		0.96-1.04	0.92-1.08	0.88-1.12	0.84-1.16	0.80-1.20		
Unmodified bitumen	unaged	26.43	48.87	72.10	87.78	96.27	1.09	8.73
	aged	39.29	64.88	75.00	80.51	82.89	1.09	9.42
Bitumen-filler mastics	unaged	25.30	47.82	65.55	76.31	84.93	1.12	11.32
	aged	12.62	25.00	35.27	45.55	57.30	1.21	19.20
Polymer-modified bit	unaged	13.69	29.46	41.43	51.13	59.05	1.25	25.63
	aged	17.37	35.19	50.19	62.75	71.96	1.16	16.03

Table 8: Goodness-of-fit for phase angle data

Sample	Condition	Discrepancy ratio, r_i					AGD	MNE
		0.96-1.04	0.92-1.08	0.88-1.12	0.84-1.16	0.80-1.20		
Unmodified bitumen	unaged	88.81	98.96	99.91	100.00	100.00	1.02	1.79
	aged	71.28	90.63	98.96	100.00	100.00	1.03	3.06
Bitumen-filler mastics	unaged	61.06	81.79	91.05	96.03	97.48	1.06	5.50
	aged	40.10	69.31	87.50	92.39	93.94	1.11	10.40
Polymer-modified bit	unaged	36.81	65.16	76.47	83.80	89.10	1.11	12.89
	aged	40.57	67.69	85.03	93.60	96.73	1.07	6.74

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