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Predictability of Complex Modulus Using Rheological Models

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Abstract: The objective of this study was to investigate the advantages and disadvantages of several linear visco-elastic rheological models applied to the unmodified and polymer-modified bitumens. It was found that all the models studied can be used to predict the linear visco-elastic of unmodified bitumens, aged and unaged samples reasonably well. In contrary, this condition was not really applicable on polymer-modified bitumens particularly for the unaged samples. The measured and predicted data was assessed using the discrepancy ratio (R_i), Mean Normalized Error (MNE) and Average Geometric Deviation (AGD) goodness of fitting statistical analysis. From the study, the modified Sigmoidal and Generalized Logistic Sigmoidal models were observed to be the most outstanding models, followed by the Christensen Anderson and Marasteanu (CAM), Christensen and Anderson (CA) and 2S2P1D (2 springs, 2 parabolic elements and 1 spring) models. The presence of semi-crystalline waves and elastomeric structures in the mixtures render the breakdown of time temperature equivalency principle.

Key words: Modeling, linear visco-elastic, complex modulus, master curve

INTRODUCTION

In principle, the complete modulus versus frequency (time of loading) behaviour of any polymer including bitumens at any temperature can be measured (Shaw and McKnight, 2005). Data can be shifted relative to the reduced frequency, so that the various curves can be aligned to form a single curve, called a master curve. The master curve represents the bitumen or asphalt mixture behaviour at a given temperature for a large range of frequencies. As discussed by Herh *et al*. (1999), the Linear Visco-Elastic (LVE) behaviour of unmodified bitumen and asphalt mixture is bounded by two main transitions. Generally, at very high frequencies/low temperatures, the elastic modulus (G_o) approaches a limiting value called the glassy state modulus. At low frequencies/high temperatures, material is behaving as the Newtonian fluid.

The principle used to relate the equivalency between frequency and temperature to construct the master curve is known as Time Temperature Superposition Principle (TTSP). The master curves can be constructed using a reference temperature (T_o) to which all data are shifted and in many cases, the T_o value can arbitrarily be chosen from one of the test

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temperature. Moreover, the amount of shifting required at each temperature to form the master curve is called the shift factor (a_T). According to Chailleux *et al.* (2006), the construction of master curves only makes sense where there should be no macromolecular structural rearrangements with temperature like phase transformations occurs and secondly, the tests are conducted in the linear visco-elastic region. A lot of attempts have been made by various researchers in developing the rheological models particularly for unmodified bitumens. However, none of the comparative studies have been made to compare all the complex modulus (|G*|) predictive equations on aged and unaged unmodified and polymer modified bitumens (PMBs) simultaneously in order to attain a better view on those equations.

In general there are two methods used for representing the Linear Viscoelastic (LVE) rheological behaviour of bitumen namely as the mathematical and mechanical models. In the mathematical (phenomenological or constitutive) approach, one is simply 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 (or analogical) approach, use is made of the fact the behaviour of linear viscoelastic material can be represented by a combination of spring and dashpot mechanical models, resulting in a particular mathematical equations. Historically, the invention of LVE rheological models is dated circa 1954 when Van der Poel developed the non-linear multivariable model called the Van der Poel's nomograph (Van-der-Poel, 1954). Since then enormous researchers showed their interest to develop the models particularly for bituminous binders and asphalt mixtures. The model can easily be constructed with the aid of Solver function in Excel spreadsheet. Solver is a powerful function to performing the nonlinear least square regression to do the fitting task in MS Excel (Pellinen *et al*., 2002). In general, a good rheological model should be able to describe as completely as possible the linear viscoelastic functions of the studied materials.

Therefore, this study was conducted to investigate the predictability of several predictive equations or models to characterize the linear visco-elastic behaviour of aged and unaged unmodified and polymer modified bitumens. Several models namely as the modified Sigmoidal, Generalized Logistic Sigmoidal, Christensen and Anderson (CA), Christensen Anderson and Marasteanu (CAM) and 2S2P1D (2 springs, 2 parabolic elements and 1 dashpot) have been used to investigate the advantages and drawbacks when the models applied to those samples. The correlation between measured and predicted values where then assessed using the goodness of fitting statistics.

RHEOLOGICAL MODELS

The Modified Sigmoidal Model

Mathematically, the |G*| equation of Sigmoidal model is shown as the following:

$$\log|G^*| = \delta + \frac{\alpha}{1+e^{\beta+\gamma\{\log(\omega)\}}} \tag{1}$$

where, log (ω) is log reduced frequency, ä is lower asymptote, α is the difference between the values upper and lower asymptote, β and γ define the shape of between the asymptotes. However, as the limiting modulus (G_o) is equal to 1GPa, the above equation can be transformed as (Garcia and Thompson, 2007):

$$\log|G^*| = \delta + \frac{\text{Max} - \delta}{1 + e^{\beta + \gamma\{\log(\omega)\}}} \tag{2}$$

where, Max is the G_o at 1 GPa (Bonaquist and Christensen, 2005). The other parameters are as previously defined.

The Generalized Logistic Sigmoidal Model

Rowe *et al*. (2008) introduced the generalization of the Sigmoid model, called the Generalized Logistic Sigmoidal model to predict the $|G^*|$ of bitumen and can be shown as the following:

$$\log|G^*| = \delta + \frac{\alpha}{\left[1 + \lambda e^{\beta + \gamma \log \omega}\right]^{1/\lambda}} \tag{3}$$

where, the parameters are as previously defined above. The λ parameter allows the curve to take a non-symmetrical shape. Like the modified Sigmoidal model, the G_o can be taken as 1GPa, therefore the following equation can be used:

$$\log|G^*| = \delta + \frac{\text{Max} - \delta}{\left[1 + \lambda e^{\beta + \gamma \log \omega}\right]^{1/\lambda}} \tag{4}$$

The Christensen Anderson Model (CA)

The $|G^*|$ equation of the Christensen and Anderson (CA) model can be presented as (Christensen and Anderson, 1992):

$$|G^*| = G_g\left[1 + (\omega_c/\omega)^{\log 2/R}\right]^{R/\log 2} \tag{5}$$

where, ω_c is the crossover frequency and R is a rheological index. The other parameters are as defined previously.

The Christensen Anderson and Marasteanu Model (CAM)

The Christensen Anderson and Marasteanu (CAM) model was developed to improve the descriptions of unmodified and modified bitumens. The $|G^*|$ equation can be shown as follows (Marasteanu and Anderson, 1999):

$$|G^*| = G_g\left[1 + (\omega_c/\omega)^{v}\right]^{\frac{w}{v}} \tag{6}$$

The introduction of w parameter addresses the issue of how fast or how slow the $|G^*|$ data converge into the two asymptotes (the 45° asymptote and the G_o asymptote) as the frequency goes to zero or infinity.

The 2S2P1D Model

The $|G^*|$ of the 2S2P1D model can be shown in the following mathematical expression (Olard and Benedetto, 2003):

$$|G^*| = G_o + \frac{G_\infty - G_o}{1 + \delta(i\omega\tau)^{k} + (i\omega\tau)^{h} + (i\omega\beta\tau)^{1}} \tag{7}$$

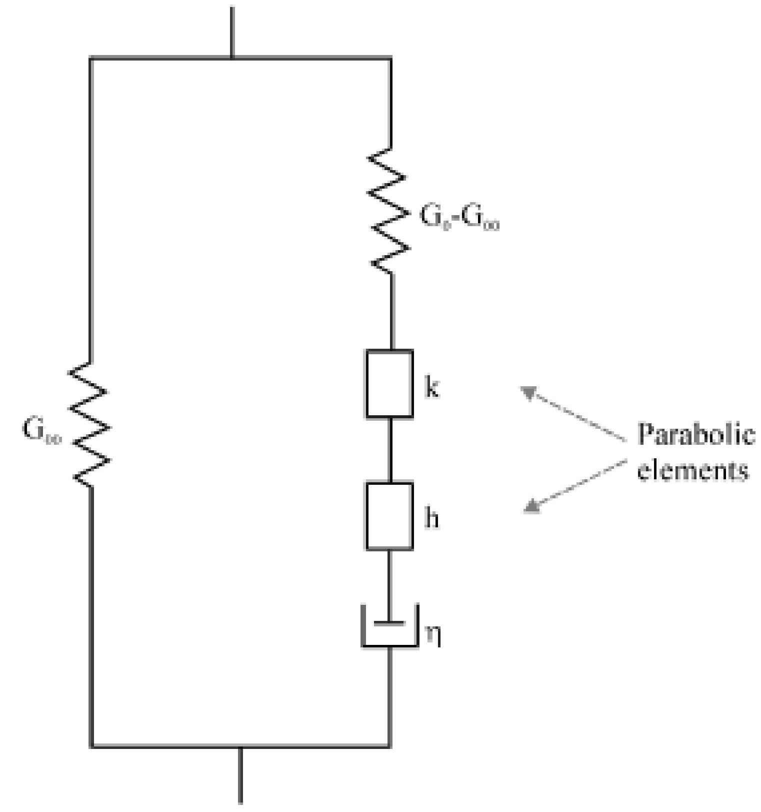

Fig. 1: The 2S2P1D model

where, i is complex number ($i^2 = -1$), ω is frequency, k and h are exponents with $0<k<h<1$,δ is constant, G_{oo} is the static modulus, G_o is the glassy modulus, β is constant and defined by $\eta = (G_{oo} - G_o)\ \beta\ \tau$, η is the Newtonian viscosity and τ is characteristic time, function of temperature. The 2S2P1D model's representation can be shown in Fig. 1.

Statistical Analysis

Three different statistical analysis have been used in this study, based on Wu *et al*. (2008):

The Discrepancy Ratio (R_i)

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

where, G^*_p and G^*_m are the predicted and measured shifting factors, respectively. The subscript i denotes the data set number. For a perfect fit, $R_i = 1$.

The Mean Normalized Error (MNE)

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

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

The Average Geometric Deviation (AGD)

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

where for a perfect fit, AGD = 1.

EXPERIMENTAL DESIGN

In this study, three different sources of bitumens i.e., from Middle East, Russian and Venezuelan were used and regarded as unmodified bitumen 70/100 penetration grade. These bitumens were blended together with ethylene-vinyl-acetate (EVA) and styrene-butadiene-styrene (SBS), respectively producing the polymer modified bitumens (PMBs) at three polymer contents, 3, 5 and 7% (by mass). All these materials underwent the dynamic shear rheometer (DSR) tests in order to obtain and evaluate the changes in their linear visco-elastic rheological properties (Airey, 2002). For the master curve construction, the T_o was arbitrarily taken at 10°C and the shifting was done manually, without assuming any functional form of the shift factor equation. The interested readers should consult Airey's research for the detail discussions on rheological characteristics of aged and unaged unmodified bitumens and PMBs.

RESULTS AND DISCUSSION

Modeling the Modified Sigmoidal Model

Three unknown parameters namely as β, δ and γ were estimated using the numerical optimization of the test data. Moreover, data at high frequency is no longer needed since the limiting of maximum modulus (G_o) of 1 GPa is specifically used. In this study, the initial guesses values are used, i.e., β = -1, δ = -1 and γ = 1. The Solver function in MS Excel then replaces the initial guesses with optimized values, as shown in Table 1 for the unaged and aged unmodified bitumens. It is observed that the δ is in negative values, showing that the moduli at low frequencies/high temperatures are small.

Meanwhile the β values, which controls the horizontal position of the turning point, decreases from unaged to aged samples regardless the source of bitumens used. This could attribute to the reason where the oxidation process occurred during ageing increases asphaltenes (polar molecules) content, therefore the samples become harder. In addition, the γ values were found to be more constant for all the samples studied. This phenomenon shows that the ageing process did not influence the steepness of the modified Sigmoidal model's slope too much. The Russian unmodified bitumen seems to have the highest parameter values. It does because it has very high sulphur content and also its asphaltene content is low and saturates are in different ratio.

The modified Sigmoidal model parameters for the unaged and aged EVA and SBS, PMBs can be shown in Table 2, however, only the Russian unmodified PMBs are shown here for brevity.

Table 1: Modified Sigmoidal model's parameters for unmodified bitumens

		Parameter		
Source	Condition	δ	β	γ
Middle East	Unaged	-4.75	-1.74	-0.29
	RTFOT	-5.35	-1.87	-0.28
	PAV	-5.91	-2.09	-0.27
Russian	Unaged	-3.98	-1.64	-0.31
	RTFOT	-4.50	-1.76	-0.30
	PAV	-5.17	-2.04	-0.28
Venezuelan	Unaged	-6.08	-1.65	-0.27
	RTFOT	-5.68	-1.74	-0.27
	PAV	-6.95	-2.02	-0.25

Table 2: Modified Sigmoidal model's parameters for polymer modified bitumens

				Parameter (s)		
Source	Condition	Modifier	Percent	δ	β	γ
Russian	Unaged	EVA	3	-5.73	-1.82	-0.26
			5	-17.87	-2.44	-0.18
			7	-57.04	-3.41	-0.14
	RTFOT		5	-11.32	-2.23	-0.21
			7	-70.88	-3.67	-0.15
	PAV		5	-8.18	-2.26	-0.23
			7	-20.15	-2.84	-0.18
	Unaged	SBS	3	-2.70	-1.53	-0.30
			5	-2.08	-1.45	-0.29
			7	-0.53	-1.20	-0.31
	RTFOT		3	-4.18	-1.78	-0.28
			5	-4.18	-1.78	-0.28
			7	-10.28	-2.11	-0.21
	PAV		3	-7.32	-2.15	-0.24
			5	-8.20	-2.18	-0.23
			7	-7.83	-2.22	-0.23

Like the unaged and aged unmodified bitumens, the ä parameter obtained for the aged and unaged PMBs are small, showing that the elastic modulus at low frequencies closely to zero. It was also observed that the present of polymer modification for unaged samples decrease the β values. In general the discussions for all modified samples are similar to the unmodified bitumens except for several samples. For instance, the difference observed between the Russian RTFOT 5 and 7% EVA PMBs were quite significant where the parameter values seem to be dispersed compare to the other samples. As discussed by Chen *et al*. (2002) the critical network might form with the modification around 5% and leads to the partial breakdown of a polymer network in the samples. Moreover, the presence of waves in certain |G*| curves cannot be predicted by the modified Sigmoidal model, suggesting that this model is not able to predict the linear visco-elastic behaviour of highly modified bitumen.

The Generalized Logistic Sigmoidal Model

As mentioned earlier, the difference between the Generalized Logistic Sigmoidal and the modified Sigmoidal models is the introduction of ë which allows the curve to take a non-symmetric shape (Rowe *et al*., 2008). The initial values for the model are used, i.e., $\delta = 0$, $\beta = 1$, $\gamma = 1$, $\lambda = 0$ and these four unknown fitting parameters are still estimated using numerical optimization of the test data. Table 3 shows the Generalized Logistic Sigmoidal model parameters obtained for the unaged and aged unmodified bitumens. Like the modified Sigmoidal function, the δ which represents the minimum |G*| values is observed to be in negative values. The β coefficient values are slightly decreased due to the samples become harder. Meanwhile, the λ values increase for the unaged and aged samples. Analysis of the materials used in this study showed that the presence of ë did not play a significant role in since its value is approaching a unity and this parameter might be useful for modeling the asphalt mixture.

Meanwhile, Table 4 shows the Generalized Logistic Sigmoidal model parameters obtained for the EVA PMBs. The small values of δ were observed at low frequencies/high temperatures. The inconsistency is detected since this model is not capable of predicting the presence of the waves curve especially at the intermediate to high temperatures in the mixture. This observation could also relate to the inconsistency of γ and λ. However, as the temperature increases, the curve reverts back to a unique slope associated with the Newtonian asymptote found for unmodified bitumens. The β are observed to be decreased

Table 3: The Generalized Logistic Sigmoidal model's parameters for unmodified bitumens

		Parameter (s)			
Source	Condition	δ	β	γ	λ
Middle East	Unaged	-6.08	-1.55	-0.26	0.96
	RTFOT	-7.38	-1.70	-0.24	0.96
	PAV	-6.56	-2.05	-0.26	0.99
Russian	Unaged	-6.58	-1.35	-0.24	0.93
	RTFOT	-4.64	-1.74	-0.29	1.00
	PAV	-5.04	-2.06	-0.29	1.00
Venezuelan	Unaged	-11.33	-1.35	-0.19	0.92
	RTFOT	-7.58	-1.63	-0.24	0.97
	PAV	-9.00	-1.96	-0.22	0.98

Table 4: The Generalized Logistic Sigmoidal model's parameters for polymer modified bitumens

				Parameter (s)			
Source	Condition	Modifier	Percent	δ	β	γ	λ
Russian	Unaged		3	-14.15	-1.40	-0.15	0.89
			5	-53.70	-2.31	-0.10	0.94
			7	-77.83	-3.16	-0.11	0.98
	RTFOT		5	-26.56	-2.29	-0.15	0.96
			7	-177.11	-4.14	-0.12	0.99
	PAV		5	-21.16	-2.52	-0.17	0.98
			7	-90.97	-3.71	-0.14	0.99
	Unaged	SBS	3	-2.86	-1.49	-0.30	0.99
			5	-3.23	-1.20	-0.25	0.94
			7	-0.22	-1.36	-0.34	1.04
	RTFOT		3	-6.02	-1.59	-0.24	0.95
			5	-6.03	-1.59	-0.24	0.95
			7	-60.68	-2.79	-0.12	0.97
	PAV		3	-11.30	-2.09	-0.20	0.97
			5	-17.91	-2.25	-0.17	0.97
			7	-46.64	-2.78	-0.13	0.97

from the unaged to the aged samples due to hardening process. The parameters of the model for the unaged and aged SBS PMBs can also be found in Table 4. The δ was also found to be in negative values as observed for the other samples. Meanwhile, the β,γ and λ were inconsistent for the SBS PMBs. This could be explained by the presence of elastomeric behaviour of SBS. The effect of ageing on the polymer dominant regions of behaviour for the SBS PMBs relate to a shifting of the rheological properties towards greater viscous response (Airey, 2002).

The Christensen and Anderson Model (CA)

In this model, the G_o was taken as 1GPa to avoid the underestimation of the value during the optimization process. Table 5 shows the CA model parameters for unaged and aged unmodified bitumens. The w_o and R were observed to be increase and decrease, respectively from the unaged to aged samples. This condition could attribute to the hardness parameters with the presence of higher asphaltenes content in aged samples. Moreover, it was observed the width of relaxation spectrum becomes smaller as the sample aged. This model, in general, predicts precisely the complex modulus at temperature of 10 to 70°C.

Meanwhile, Table 6 shows the CA parameters for the unaged and aged EVA PMBs. Generally, the w_o coefficient values are increased from unaged to aged samples and on the other hand, the width of relaxation spectrum becomes smaller. This behaviour give supports to some authors who relate the R to the binder asphaltene content, finding that it grows as this polar molecules is elated (Silva *et al*., 2004). However, like the previous models, this model was also not able to predict the presence of special importance elements such as the semi-crystalline structure in EVA PMBs and elastomeric SBS PMBs.

Table 5: The CA model's parameters for unmodified bitumens

Source	Condition	Parameter (s) G_o	Log 2	w_o	R
Middle East	Unaged	1E+09	0.30	1.36	10.79
	RTFOT	1E+09	0.30	1.48	4.47
	PAV	1E+09	0.30	1.67	0.58
Russian	Unaged	1E+09	0.30	1.29	18.55
	RTFOT	1E+09	0.30	1.43	7.19
	PAV	1E+09	0.30	1.55	0.98
Venezuelan	Unaged	1E+09	0.30	1.33	43.28
	RTFOT	1E+09	0.30	1.55	10.05
	PAV	1E+09	0.30	1.79	0.98

Table 6: The CA model's parameters for polymer modified bitumens

Source	Condition	Modifier	Percent	Parameter (s) G_o	Log 2	w_o	R
Venezuelan	Unaged	EVA	3	1E+09	0.30	1.80	6.25
			5	1E+09	0.30	2.24	0.74
			7	1E+09	0.30	2.74	0.11
	RTFOT		5	1E+09	0.30	2.40	0.14
			7	1E+09	0.30	2.99	0.02
	PAV		5	1E+09	0.30	2.70	0.01
			7	1E+09	0.30	3.20	0.00
	Unaged	SBS	3	1E+09	0.30	1.78	7.53
			5	1E+09	0.30	2.03	2.45
			7	1E+09	0.30	2.21	0.83
	RTFOT		3	1E+09	0.30	1.94	2.20
			5	1E+09	0.30	2.25	0.74
			7	1E+09	0.30	2.36	0.25
	PAV		3	1E+09	0.30	2.22	0.13
			5	1E+09	0.30	1.98	0.70
			7	1E+09	0.30	2.70	0.01

Table 7: The CAM model's parameters for unmodified bitumens

Source	Condition	Parameter (s) G_o	Log 2	v	w	w_c	R
Middle East	Unaged	1E+09	0.30	0.17	1.09	1.26	1.78
	RTFOT	1E+09	0.30	0.16	1.11	0.40	1.89
	PAV	1E+09	0.30	0.14	1.20	0.01	2.20
Russian	Unaged	1E+09	0.30	0.18	1.08	3.63	1.63
	RTFOT	1E+09	0.30	0.17	1.10	0.96	1.79
	PAV	1E+09	0.30	0.15	1.14	0.05	1.98
Venezuelan	Unaged	1E+09	0.30	0.17	1.10	4.40	1.81
	RTFOT	1E+09	0.30	0.15	1.14	0.55	2.03
	PAV	1E+09	0.30	0.13	1.23	0.01	2.39

The CAM Model

The CAM model was proposed to improve the CA model and by comparing these two models, it can be noted that the Log 2/R is equivalent to the v of the CAM model (Silva *et al*., 2004). In this study, the glassy modulus was taken as 1 GPa for all unaged and aged samples. The CAM model coefficients for the unaged and aged unmodified bitumens can be shown as in Table 7.

It was observed that the v and R values decrease and increase, respectively, from unaged to aged unmodified bitumens. As frequency approach zero, the PAV aged samples reaches the 45° asymptote faster than unaged bitumens. The w_c values are decreased from unaged to aged bitumens, suggesting that samples become stiffer due to the ageing process. Meanwhile, Table 8 shows the CAM model parameters for the EVA and SBS PMBs, aged and unaged, respectively. The v values for all samples except the PAV Middle East EVA PMBs

Table 8: The CAM model's parameters for polymer modified bitumens

Source	Condition	Modifier	Percent	Parameter (s)					
				G_o	Log 2	v	w	w_c	R
Middle East	Unaged	EVA	3	1E+09	0.30	0.16	1.07	0.94	1.85
			5	1E+09	0.30	0.16	1.00	0.96	1.92
			7	1E+09	0.30	0.16	0.95	0.95	1.91
	RTFOT		3	1E+09	0.30	0.17	1.02	0.94	1.76
			5	1E+09	0.30	0.17	0.96	0.94	1.75
			7	1E+09	0.30	0.15	0.91	0.94	1.98
	PAV		3	1E+09	0.30	0.20	0.93	0.94	1.68
			5	1E+09	0.30	0.14	0.97	0.94	2.10
			7	1E+09	0.30	0.15	0.84	0.45	1.98
Venezuelan	Unaged	SBS	3	1E+09	0.30	0.13	1.16	0.22	2.31
			5	1E+09	0.30	0.13	1.11	0.19	2.38
			7	1E+09	0.30	0.13	1.06	0.19	2.40
	RTFOT		3	1E+09	0.30	0.15	1.04	0.97	2.04
			5	1E+09	0.30	0.14	0.99	0.97	2.20
			7	1E+09	0.30	0.14	0.93	0.97	2.16
	PAV		3	1E+09	0.30	0.16	0.93	0.95	1.92
			5	1E+09	0.30	0.16	1.00	0.89	1.94
			7	1E+09	0.30	0.14	0.84	0.97	2.12

Table 9: The 2S2P1D model's parameters for unmodified bitumens

Source	Condition	Parameter (s)						
		G_{oo} (Pa)	G_g (Pa)	k	h	δ	τ	β
Middle East	Unaged	0	1E+09	0.21	0.55	2.3	5.0E-05	300
	RTFOT	0	1E+09	0.21	0.55	4.0	7.0E-05	700
	PAV	0	1E+09	0.21	0.55	5.0	4.0E-04	1000
Russian	Unaged	0	1E+09	0.21	0.55	3.5	5.0E-05	150
	RTFOT	0	1E+09	0.21	0.55	5.0	5.0E-05	400
	PAV	0	1E+09	0.21	0.55	5.0	4.0E-04	1500
Venezuelan	Unaged	0	1E+09	0.21	0.55	2.3	1.5E-05	200
	RTFOT	0	1E+09	0.21	0.55	3.5	3.2E-05	500
	PAV	0	1E+09	0.21	0.55	4.5	1.0E-04	1500

show constant value with the modification of 3 to 7%. Moreover, the R values increase as the asphaltenes content increases. In contrast, the w is decrease from 3 to 7%, showing the 3% of modification reaches the 45° asymptote faster than the 7% with the lower value.

The 2S2P1D Model

Table 9 shows the 2S2P1D model parameters for all bitumens used in this study. The G_{oo} is equal to zero and only six constants of the model are needed to be determined. It was observed that the G_{oo}, G_o, k and h are consistent for all studied materials.

Moreover, it was found that the β linked to the Newtonian viscosity η of the model has a large influence in this domain of behaviour. The influence of the binder ageing affects the β, where this parameter keeps increased from unaged to the aged. As the materials become harder, the δ values increased. The 2S2P1D model parameters for EVA and SBS PMBs are shown in Table 10. The δ was found to be more consistent for the SBS PMBs compared to the EVA PMBs. This is probably due to the fact that the presence of crystalline structure at different temperatures increases the complexity of the bitumens. Moreover, the DSR compliance errors may also occur for PMBs samples. As the percentage of the modifier is elevated, the β increases. Like the other samples, for the aged samples the G_{oo}, G_o, k and h parameters can be taken similar for all studied samples.

Table 10: The 2S2P1D model's parameters for polymer modified bitumens

				Parameter (s)						
Source	Condition	Modifier	Percent	G_{oo} (Pa)	G_o (Pa)	k	h	δ	τ	β
Middle East	Unaged	EVA	3	0	1E+09	0.21	0.55	3.5	7.0E-05	900
			5	0	1E+09	0.21	0.55	5.0	7.0E-05	2500
			7	0	1E+09	0.21	0.55	5.0	1.0E-04	6000
	RTFOT		3	0	1E+09	0.21	0.55	4.5	1.0E-04	1500
			5	0	1E+09	0.21	0.55	5.0	3.0E-04	2000
			7	0	1E+09	0.21	0.55	5.0	2.0E-04	10000
	PAV		3	0	1E+09	0.21	0.55	7.0	5.0E-04	2500
			5	0	1E+09	0.21	0.55	7.0	2.0E-03	3000
			7	0	1E+09	0.21	0.55	7.0	2.0E-03	10000
Russian	Unaged	SBS	3	0	1E+09	0.21	0.55	2.3	3.0E-05	1500
			5	0	1E+09	0.21	0.55	2.3	3.0E-05	3000
			7	0	1E+09	0.21	0.55	2.3	5.0E-06	20000
	RTFOT		3	0	1E+09	0.21	0.55	5.0	8.0E-05	1500
			5	0	1E+09	0.21	0.55	5.0	9.0E-05	1000
			7	0	1E+09	0.21	0.55	5.0	3.0E-05	5000
	PAV		3	0	1E+09	0.21	0.55	7.0	4.5E-04	1500
			5	0	1E+09	0.21	0.55	7.0	2.0E-04	3000
			7	0	1E+09	0.21	0.55	5.0	3.0E-04	5000

Statistical Analysis

To evaluate the performance of the predictive equation, the correlation of the measured and predicted values was assessed using the R_i, MNE and AGD. The R_i is used to observe the predicted data's dispersion from the equality line, with one as the perfect value. In this study, the interval of 2% from the equality line was used until R_i reaches interval of 10%. Table 11 shows the goodness of fit statistics for the unaged and aged unmodified bitumens. It was observed that all of the models studied show a good correlation when the R_i = 0.95- 1.05. This finding indicates that all of the LVE rheological models used in this study can predict the aged and unaged unmodified bitumens precisely. However, the modified Sigmoidal model shows the most outstanding correlation, followed by the Generalized Logistic Sigmoidal, CAM and CA models. On the other hand, the 2S2P1D model seems to have the worst correlation. This could attribute to the reason where during the modeling work, the compliance error from the DSR machine was taking into account, therefore the predicted |G*| values were slightly higher compare to the experimental data at high frequencies. Moreover, each of this model parameter has a direct relation with the construction of |G*| master curve, the Black diagram and also the Cole-Cole diagram. Conversely, the other models used only rely on the construction of |G*| master curve.

The modified Sigmoidal, Generalized Logistic Sigmoidal and CAM models show the best correlation with 10% of R_i for the aged unmodified bitumens. However, it also showed that the CA and 2S2P1D models data tabulated closely to the equality line. The Generalized Logistic Sigmoidal model shows the best correlation, showing the presence of ë plays a significant role for the aged samples. Meanwhile the modified Sigmoidal and CAM models also predict the measured data really well. Interestingly, the 2S2P1D model shows better correlation compare to the CA model. This finding was in good agreement with the previous study where the CA model was not able to predict the linear visco-elastic properties of bitumens particularly at higher and lower temperatures (Christensen and Anderson, 1992).

It was observed that for the unaged PMBs (Table 12), the Generalized Logistic Sigmoidal and modified Sigmoidal models had comparably good results, followed by the CAM, CA and 2S2P1D models. However, the modified Sigmoidal model predicts the behaviour of PMBs in better way with the lowest AGD and highest MNE values, respectively. This indicates that

Table 11: Goodness of fit statistical analysis for the unmodified bitumens

		Discrepancy ratio (R_i)								
Model	Condition	0.99-1.01	0.98-1.02	0.97-1.03	0.96-1.04	0.95-1.05	S_e/S_y	R^2	AGD	MNE
Modified Sigmoidal	Unaged	89.13	97.52	99.07	99.38	99.38	0.0180	0.9997	1.0059	0.5819
Modified Richards		95.65	97.83	99.07	99.38	99.38	0.0092	0.9999	1.0035	0.3446
CA		84.78	98.45	99.07	99.38	99.38	0.0170	0.9997	1.0053	0.5269
CAM		96.27	98.14	98.76	99.07	99.38	0.0102	0.9999	1.0041	0.4111
2S2P1D		72.05	94.10	97.83	97.83	97.83	0.0209	0.9996	1.0084	0.8401
Modified Aigmoidal	Aged	96.43	98.96	99.55	100.00	100.00	0.0139	0.9998	1.0029	0.2892
Modified richards		97.32	98.96	99.70	100.00	100.00	0.0119	0.9999	1.0025	0.2487
CA		59.67	92.11	98.81	99.41	99.70	0.0342	0.9988	1.0095	0.9412
CAM		95.83	99.11	99.70	99.85	100.00	0.0145	0.9998	1.0033	0.3300
2S2P1D		73.07	85.86	95.39	97.92	98.96	0.0315	0.9990	1.0089	0.8986

Table 12: Goodness of fit statistical analysis for the polymer modified bitumens

		Discrepancy ratio (R_i)								
Model	Condition	0.99-1.01	0.98-1.02	0.97-1.03	0.96-1.04	0.95-1.05	S_e/S_y	R^2	AGD	MNE
Modified Sigmoidal	Unaged	65.42	83.51	90.83	94.76	97.32	0.0476	0.9977	1.0115	1.1388
Modified Richards		74.23	86.96	92.50	95.66	97.50	0.0376	0.9986	1.0097	0.9595
CA		50.95	75.00	85.24	90.24	92.86	0.0572	0.9967	1.0171	1.6771
CAM		56.43	79.94	89.52	93.75	95.71	0.0479	0.9977	1.0141	1.3889
2S2P1D		35.66	59.64	73.69	82.68	86.01	0.0859	0.9926	1.0262	2.5778
Sigmoidal	Aged	80.36	95.36	98.56	99.52	99.79	0.0315	0.9990	1.0067	0.6692
Richards		88.61	96.29	98.62	99.42	99.76	0.0242	0.9994	1.0051	0.5071
CA		70.83	90.95	96.63	97.87	99.00	0.0345	0.9988	1.0087	0.8659
CAM		54.52	80.01	89.75	93.57	95.73	0.1463	0.9786	1.0173	1.6316
2S2P1D		49.02	78.36	88.55	93.67	96.08	0.0551	0.9970	1.0150	1.5037

the addition of ë in generalized logistic sigmoidal did not play a significant role in predicting the linear visco-elastic behaviour of PMBs. Meanwhile, the 2S2P1D model shows the worst correlation where the predicted data seems dispersed from the equality line. As discussed by Olard and Di Benedetto, this model was not suitable to be used and from their study, it only conform behaviour of PMBs at low temperature (Olard and Benedetto, 2003). The Generalized Logistic Sigmoidal shows the best correlation in term of MNE for the aged PMBs, even though it has comparable values for the R_i at 0.95-1.05 and AGD with the modified Sigmoidal model. The CA model also shows good correlation with the values of MNE and AGD. This could attribute to the reason where the CAM model cannot predict the complexity behaviour of the aged PMBs. In general, all of the LVE rheological models suffer from similar drawbacks where they cannot predict the linear visco-elastic behaviour of unaged and aged PMBs precisely. The presence of semi-crystalline EVA and SBS modified can be linked to the breakdown of the molecular structure of the copolymer to form a lower molecular weight polymer substructure changes the rheological properties of materials (Airey, 2002).

CONCLUSIONS

Several conclusions can be drawn from the study as:

- It was observed that all the linear visco-elastic (LVE) rheological models are able to predict the unaged and aged unmodified bitumens satisfactorily. For modeling purposes, the glassy modulus for unmodified and polymer modified bitumens (PMBs), aged and unaged samples, approaching the value of 1 GPa. Moreover, the elastic modulus (G_{∞}) value is really small and in most cases, this value can be neglected

- However, these predictive models suffer from the drawback where they did not able to predict the linear visco-elastic behaviour particularly for the unaged PMBs due to the presence of semi-crystalline EVA and SBS modified, rendering the breakdown in time temperature superposition principle
- For the unaged and aged unmodified bitumens, the modified Sigmoidal and Generalized Logistic Sigmoidal models were shown to be the best models, followed by the CAM, CA and 2S2P1D models. In addition, the Generalized Logistic Sigmoidal and modified Sigmoidal models show the most outstanding correlations for the unaged and aged PMBs
- The CAM model improves the CA model curve fitting particularly at extreme zones of complex modulus master curve
- The presence of additional λ parameters in modified generalized logistic sigmoidal model which cater for the non-symmetrical shape of the curve seems did not play a significant role since shape of the complex modulus master curves were not too different from each other. This model might suitable to be used for the asphalt mixture and in many cases of bituminous binders, the modified Sigmoidal model is appropriate
- The 2S2P1D model was statistically observed to be the worst model compares to the others, but this model still can be thought as a unique rheological model. The model consists of seven unknown parameters, relates to the construction of the complex modulus master curve, the Black and Cole-Cole diagrams. In contrast, the other models coefficients merely related to the construction of complex modulus master curves

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REFERENCES

Airey, G.D., 2002. Use of black diagrams to identify inconsistencies in rheological data. Road Materials Pav. Design, 3: 403-424.

Bonaquist, R. and D.W. Christensen, 2005. Practical procedure for developing dynamic modulus master curves for pavement structural design. Transport Res. Rec., 1929: 208-217.

Chailleux, E., G. Ramond and C.D.L. Roche, 2006. A mathematical-based master curve construction method applied to complex modulus of bituminous materials. Road Mater. Pav. Des., 7: 75-92.

Chen, J.S., M.. Liao and H.H. Tasi, 2002. Evaluation and optimization of the engineering properties of polymer-modified asphalt. J. Failure Anal. Prevention, 2: 75-83.

Christensen, D.W. and D.A. Anderson, 1992. Interpretation of dynamic mechanical test data for paving grade asphalt caments. J. Assoc. Asphalt Paving. Technol., 61: 67-116.

Garcia, G. and M. Thompson, 2007. HMA dynamic modulus predictive models: A review. Research Report FHWA-ICT-07-2005. Illinois Centre for Transportation. http://ict.illinois.edu/Publications/report%20files/FHWA-ICT-07-006.pdf.

Herh, P.K.W., S.M. Colo and B.K.S. Rudolph, 1999. Dynamic shear rheometers pave the way for quality asphalt binders. Application Note. Rheo Logica Instruments. http://www.atsrheosystems.com/PDF%20files/Asphalt%20Paper.pdf.

Marasteanu, O. and D.A. Anderson, 1999. Improved model for bitumen rheological characterization. Eurobitume Workshop on Performance Related Properties for Bituminous Binder, Luxembourg, Paper No. 133.

Olard, F. and H.D. Benedetto, 2003. General 2S2P1D model and relation between the linear visco-elastic behaviours of bituminous binders and mixes. J. Road Mater. Pav. Des., 4: 185-224.

Pellinen, T.K, M.W. Witczak and R.F. Bonaquist, 2002. Asphalt mix master curve construction using sigmoidal fitting function with non-linear least squares optimization technique. Proceedings of 15th ASCE Engineering Mechanics Conference, June 2-5, Columbia University, New York, pp: 83-101.

Rowe, G.M., G. Baugmgardner and M.J. Sharrock, 2008. A generalized logistic function to describe the master curve stiffness properties of binder mastics and mixtures. 45th Petersen Asphalt Research Conference, Laramie, Wyoming, July 14-16 2008. http://www.abatech.com/documents/Master%20Curve.pdf.

Shaw, M. and W.J. McKnight, 2005. Introduction to Polymer Visco-Elasticity. 3rd Edn., John Wiley and Sons, New York, USA.

Silva, L.S.D., M.M.D.C. Forte, L.D.A. Vignol and N.S.M. Cardozo, 2004. Study of rheological properties of pure and polymer modified Brazilian asphalt binders. J. Mat. Sci., 39: 539-546.

Van-der-Poel, C., 1954. A general system describing the visco-elastic properties of bitumens and its relation to routine test data. J. Applied Chem., 4: 221-236.

Wu, B., A. Molinas and P.Y. Juliean, 2008. Predictability of sediment transport in the yellow river using selected transport formulas. Int. J. Sediment Res., 23: 283-298.