A mathematical-based master-curve construction method applied to complex modulus of bituminous materials

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ABSTRACT. *This paper gives a mathematical-based procedure in order to construct master-curves from complex-modulus measurements. The method is based on the Kramers-Kronig relations linking modulus and phase angle of a complex function. Three pure bitumens, one polymer-modified-binder and two mixtures are chosen to validate the possible use of this methodology and apply it. Assumptions which are needed to apply this procedure, are verified on complex-modulus data measured from these materials. Hence, master-curves can be built without introducing error from manual adjustement. The method seems to be suitable for binders and mixtures as soon as their behaviour is in agreement with the time-temperature equivalency principle. In conclusion, some interpretations of the WLF constants are given.*

KEYWORDS: *master-curve, Kramers-Kronig, WLF, bitumens, bituminous mixtures.*

1. Introduction

Rheology of bituminous materials is strongly dependent of loading time and temperature. Interrelationship between frequency and temperature for these materials makes possible to get the same mechanical behaviour in different experimental conditions. Hence, mechanical properties, determined at high loading time (or low frequency) and at low temperature, can be found at low loading time (or high frequency) and at high temperature. In some cases (thermo rheologically simple bituminous materials) the equivalency between time and temperature allows to build master curve from linear viscoelastic data by shifting measurement at different temperature in order to obtain a continuous curve at a reference temperature. This method commonly applied for polymers (Ferry, 1980) is also suitable for bituminous materials (Goodrich, 1988; Ramond *et al.*, 2003; Dobson, 1969). When this time-temperature-principle can be applied, master-curve construction from viscoelastic parameters, modulus ($|G^*|$ or $|E^*|$) and phase angle (δ), allows to obtain materials behaviour on a time and temperature scale larger than the one which is measurable. However, shift factors are most of the time determined by adjusting adjacent isotherms. In this way, errors can occur due to the fitting procedures and criteria, especially when isotherms do not overlap.

This paper describes a mathematical-based procedure to construct master curve from complex modulus. We propose to apply this method, first used for binders (Ramond *et al.*, 2003), for mixtures and to build a tool to compare viscoelastic properties of bituminous materials. It is based on the Kramers-Kronig relation linking real part and imaginary part of a complex function. This procedure allows to draw master-curve at any measured reference temperature. The use, in addition, of the WLF constants allows to construct them at any temperature.

2. Theoretical approach of the master curve construction

2.1. *Interrelation between viscoelastic functions*

Kramers-Kronig relations are the integral transform relationships between the real and imaginary parts of a complex function. These relations which are true for function meeting Bolzman superposition principle and causality principle, can be applied for complex modulus. Hence, H. C. Booij (Booij *et al.*, 1982) showed that for shear complex modulus defined as:

$$G^*(i\omega) = G'(\omega) + iG''(\omega) = |G^*|\, e^{i\delta(\omega)} \tag{1}$$

Kramers-Kronig relations give the following equations:

$$log|G^*(\omega)| - log|G^*(\infty)| = -\frac{2}{\pi} \int_0^\infty \frac{u \cdot \delta(u) - \omega \cdot \delta(\omega)}{u^2 - \omega^2} du \tag{2}$$

$$\delta(\omega) = \frac{2\omega}{\pi} \int_0^\infty \frac{log|G^*(u)| - log|G^*(\omega)|}{u^2 - \omega^2} du \qquad [3]$$

By simplifying equation [3] and testing the result on experiments carried out on a polyvinylacetate sample with a mechanical spectrometrer, Booij finally gives the following approximation [4]:

$$\delta(\omega) \approx \frac{\pi}{2} \frac{dlog(|G^*(\omega)|)}{dlog(\omega)} \qquad [4]$$

It could be demonstrated (Stefani, 2001) that if material behaviour fits parabolic creep :

$$f(t) = A \cdot t^\alpha \qquad [5]$$

approximation [4] becomes exact:

$$\delta(\omega) = \frac{\pi}{2} \frac{dlog(|G^*(\omega)|)}{dlog(\omega)} \qquad [6]$$

2.2. *Validity conditions for master curve construction*

Master curve construction only makes sense if there are no macromolecular structural rearrangements with temperature like phase transformations and if the tests are performed in the linear viscoelastic region. In this case, Black Diagram ($\delta = f°(|G^*|)$) draws a continuous curve which means that isotherms overlap themselves (material is thermo rheologically simple). In a close neighborhood, at one angle δ corresponds only one value of modulus. Smoothness of this curve allows to say that a mechanical behaviour (based on the modulus and phase angle evaluation) can be obtained for different temperature and frequency loadings, this is the time-temperature equivalency.

Shift factor a_T which is needed to get the same modulus for different loading conditions is defined as follow:

$$G^*(T_i, f_i) = G^*(T_j, f_j = a_{(T_i, T_j)} \cdot f_i) \qquad [7]$$

Figure 1 represents a Black Diagram for a pure bitumen. As we can see, the curve is continuous. Isotherms have some common points. In this typical case, the time temperature equivalence principle can be applied.
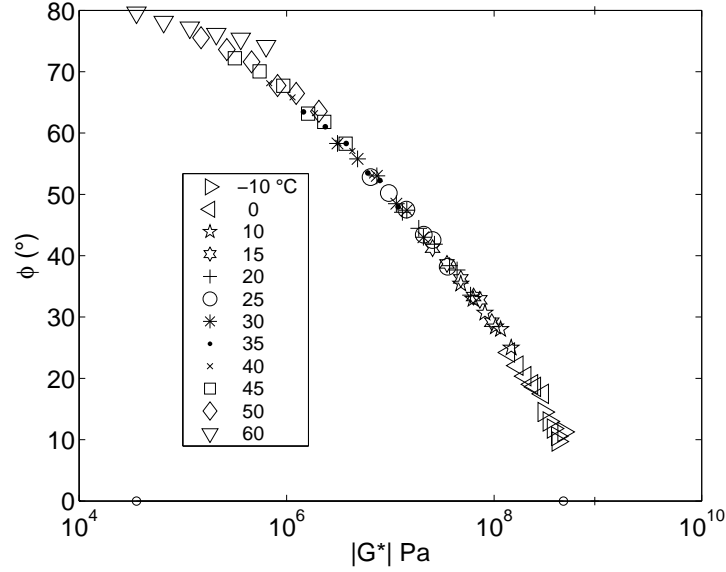
Figure 1. *Black diagram for a pure bitumen measured on a METRAVIB visco-analysor*

2.3. *Determination of translation factors* a_T

The relation [6] can be used to get the shift factors. In fact, if two close frequencies are considered ω_i and ω_j ($\omega = 2 \cdot \pi \cdot f$), we can write:

$$\delta_{avr}^{(\omega_i, \omega_j)} \cdot \frac{2}{\pi} = \frac{log(|G^*(T, \omega_j)|) - log(|G^*(T, \omega_i)|)}{log(\omega_j) - log(\omega_i)} \qquad [8]$$

Where $\delta_{avr}^{(\omega_i, \omega_j)}$ is the average of two angles measured at ω_i and ω_j (for temperature T). Better approximation could also be made by performing an interpolation of δ according to temperature.

Considering that the time temperature equivalency principle can be applied, a shift factor exists: $a_{(T_1, T_2)} = f_2/f_1 = \omega_2/\omega_1$ such as $|G^*(T_1, \omega_1)| = |G^*(T_2, \omega_2)|$.

Hence, for two close temperatures, relation [8] can be written:

$$\delta_{avr}^{(T_1, T_2)}(\omega_2) \cdot \frac{2}{\pi} = \frac{log(|G^*(T_1, \omega_2)|) - log(|G^*(T_2, \omega_2)|)}{log(a_{(T_1, T_2)})} \qquad [9]$$

Where $\delta_{avr}^{(T_1, T_2)}$ is the average of two angles measured at T_1 and T_2 (for ω_2).

Therefore, shift factors can be calculated using equation [9] gradually for close isotherms, at only one frequency. Considering that measurements are carried out at temperature $T_1, T_2, ..., T_i, T_{i+1}, ..., Tn$, master curve construction related to a reference temperature T_{ref} (with ref between 1 and n) will be made using cumulative sum of $log(a_{(T_i, T_{i+1})})$. Hence, shift factor, needed to be applied for an isotherm T_i according the reference temperature T_{ref}, will be:

$$log(a_{(T_i, T_{ref})}) = \sum_{j=i}^{j=ref} log(a_{(T_j, T_{j+1})})$$ [10]

then,

$$log(a_{(T_i, T_{ref})}) = \sum_{j=i}^{j=ref} \frac{log(|G^*(T_j, \omega)|) - log(|G^*(T_{j+1}, \omega)|)}{\delta_{avr}^{(T_j, T_{j+1})}(\omega)} \cdot \frac{\pi}{2}$$ [11]

This is worth noting that it will be necessary to verify equation [8] from viscoelastic data measurement before applying this process.

2.4. *Construction of master-curve for a non measured temperature*

In order to build a master-curve at any reference temperature, a law to model $a_T(T)$ is needed. The Williams Landel and Ferry (WLF) equation [12] proposed to model shift factors for polymers (Ferry, 1980) was also applied successfully for bituminous materials (Jongepier *et al.*, 1969; Dobson, 1969; Olard *et al.*, 2003; Ramond *et al.*, 2003). But, it is also possible to use Arrhenius law if the WLF law does not allow to fit the calculated shift factors (Francken *et al.*, 1998).

$$log(a_{(T_i, T_{ref})}) = \frac{-c_1^{ref} \cdot (T_i - T_{ref})}{c_2^{ref} + T_i - T_{ref}}$$ [12]

With the approximation [11], it is possible to construct master curve from data at a reference temperature T_{ref} that is really measured. Nevertheless, in order to be able to get shifts factor at any reference temperatures $T_{ref'}$, Ferry (Ferry, 1980) underlines that the form of equation [12] is independent of the choice of T_{ref}. Then, equation [12] can be written with an other reference temperature $T_{ref'}$, but associated with other constants: $c_1^{ref'}$ and $c_2^{ref'}$. It can be demonstrated (from equation [12] written at T_{ref} and $T_{ref'}$) that relations between these constants are:

$$c_2^{ref} = c_2^{ref'} + T_{ref} - T_{ref'}$$ [13]

$$c_1^{ref} = \frac{c_1^{ref'} \cdot c_2^{ref'}}{c_2^{ref}} \qquad [14]$$

Finally, it will be only necessary to determine c_1^{ref} and c_2^{ref} at T_{ref} to be able to construct master curves at any temperature.

3. Experimental part: rational master curve construction applied to bituminous materials

3.1. *Experimental set-up*

3.1.1. *Dynamical Mechanical Analysis*

In order to identify the linear viscoelastic behaviour of binders and mixtures two test set-ups are used, respectively a viscoanalysor METRAVIB (see figure 2(a)) and a MLPC complex modulus device (see figure 2(b)).

Two modes of loading are used for binders: annular shearing for high temperatures [25°C ; 80°C] and tension-compression for low temperatures [-20°C ; 20°C]. Shear Modulus G^* given by the annular shearing experiment is converted into tension-compression modulus E^* using a poisson ratio equal to 0.5.

Regarding mixtures, experiments are carried out on trapezoïdal samples according to the NF EN 12697-26 standard.

Testing mode for binders are strain controlled mode and stress controlled mode for mixtures. Experimental conditions are summarized on the table 1.

Table 1. *Test conditions for the viscoelastic measurements*

Device	METRAVIB	METRAVIB	MLPC
loading mode	annular-shearing	tension-compression	2 points bending
Frequencies	7.8 - 250 Hz	7.8 - 250 Hz	1 - 30 Hz
Max strain	0.45%	0.03%	0.005%
Temperature	[25°C ; 80°C]	[-20°C ; 20°C]	[-10°C ; 40°C]

3.1.2. *Materials*

Four binders and two bituminous mixtures are chosen to apply the mathematical-based master-curve contruction (see table 2). Three of these binders are pure bitumens (10/20, 20/30 and 50/70) and the last one is a modified polymer bitumen with SBS (5%). Both Mixtures have the same aggregate composition (see figure 3) and binder content (5.3% per 100% aggregates). The binders used for the mixtures are both pure bitumens B2 and B3 (20/30, 50/70) mentioned previously.
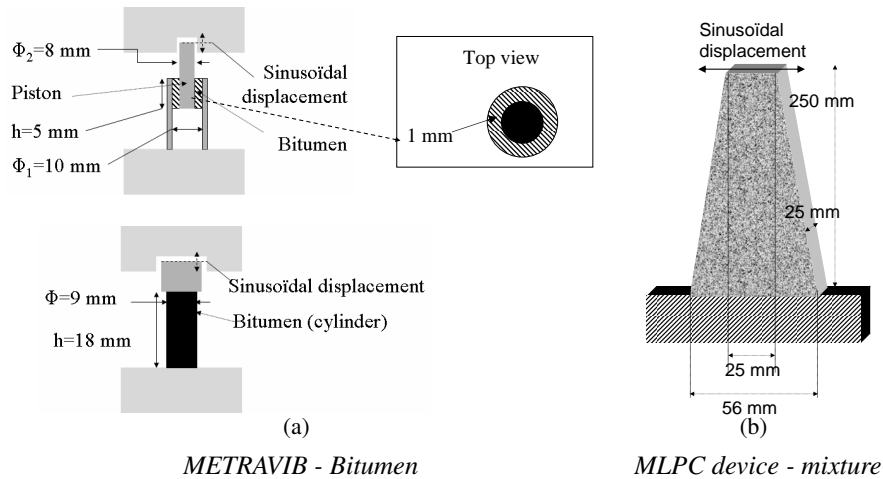
(a)

METRAVIB - Bitumen

(b)

MLPC device - mixture

Figure 2. *Shematic of the two modes of loading used with the viscoanalysor ME-TRAVIB: annular shearing and tension-compression, and the two point bending test used for mixture*

Table 2. *Materials used for viscoelastic analysis*

Binder	Mixture
B1 - pure 10/20	
B2 - pure 20/30	M1 - BBSG 0/14 (binder B2 20/30)
B3 - pure 50/70	M2 - BBSG 0/14 (binder B3 50/70)
B4 - PmB SBS 5%	

4. Verification of the hypothesis and construction of the master curves

4.1. *Verification of the relation [8]*

In order to verify the Booij equation [6] and consequently the Kramers-Kronigs relations, we propose to plot $dlog(|G^*(\omega)|)/dlog(\omega)$ according to $\delta/90$. Relation [8] is used to make the calculation for each temperature taking two by two the closest frequencies. The figures 4(a) and 4(b) depict the result of this calculation for the bitumen 50/70 tested after RTFOT and for the mixture M1. From these results, we can say that the equation [6] is validated (standard deviation calculated at the lowest frequency is $7.5 \cdot 10^{-4}$ for M1 and $5.3 \cdot 10^{-3}$ for B3). A systematic verification carried out on all samples confirms that Booij approximation can be applied with bituminous materials chosen for this study. However, measurements at the highest frequencies seem to diverge from the Kramers-Kronigs relation. It is still to investigated if this
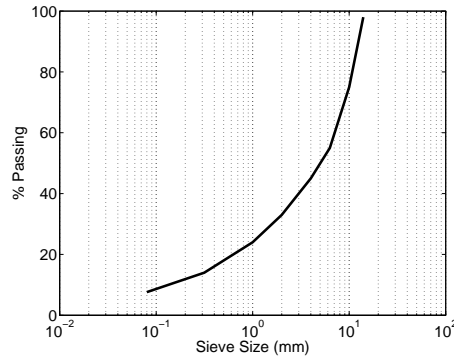
Figure 3. *BBSG 0/14 mixture grading*

result reflects a non-linearity of the materials or if these high frequency measurements show a lack of precision.

### 4.2. *Master curve construction for binders*

The viscoelastic data which were measured according to the experimental conditions described in the section 3.1 are drawn on figures 5(a) and 5(b). Black diagram does not allow to find differences between pure bitumens. Only the Pmb binder shows a typical relaxation in the quasi-liquid state. Cole-cole curves reflect the penetration grade of the bitumens. It appears that the Pmb binder seems to be very close to the 50/70 pure bitumen in the glassy state.

The procedure described in the section 2.3 is applied to these viscoelastic data. The shift factors at a reference temperature of $0°C$ is calculated from equation [11]. The results are depicted on figures 6(a) and 6(b). Modulus and Angle master-curves show continuous curves for all the bitumens. It has to be pointed out that even if an isotherm is missing (see bitumen B1 on the cole-cole curve) the rational procedure is able to adjust the shift factor in an accurate way.

On the other hand, the ranking of the binders given by the master curve agrees with their penetration grade. At a given frequency, the 10/20 bitumen is the stiffest and its phase angle is the smallest. Pmb Bitumen B4 master curve matches with the B3 curves in the glassy state.

4.3. *Master curve construction for mixtures*

Thermal dependence of bituminous mix is dominated by the thermo-mechanical behaviour of the binders. Therefore, it seems that the procedure to construct master curve applied for bitumen should also suit for mixtures. We verify (figures 7(a)
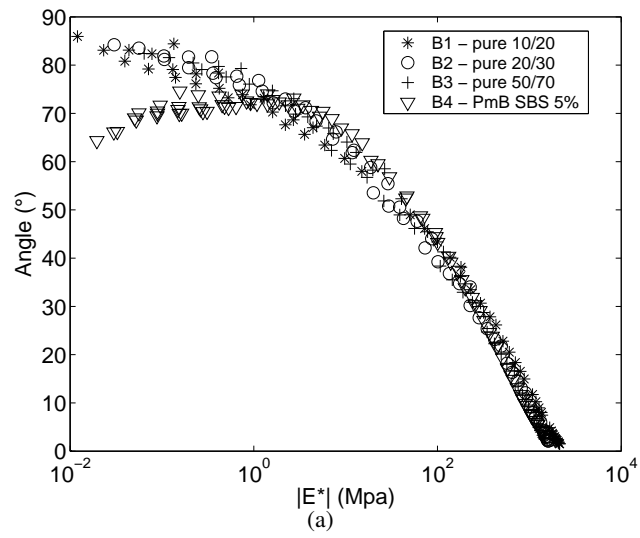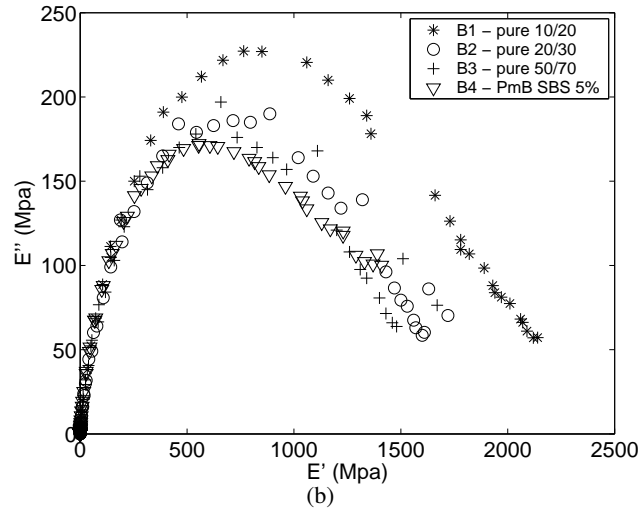
(a)
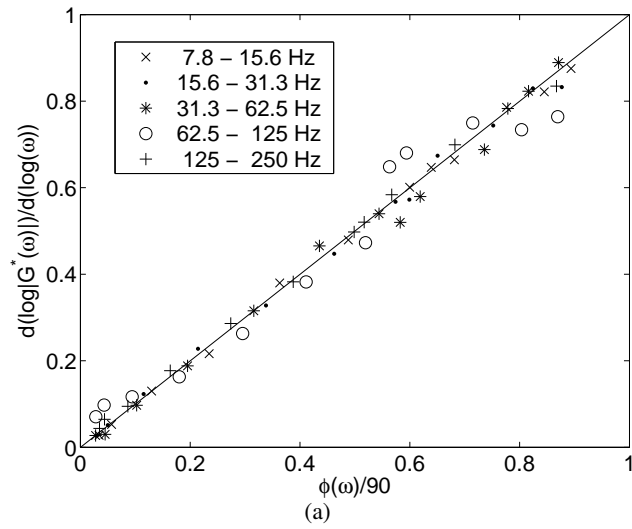
B3 binder after RTFOT

(b)
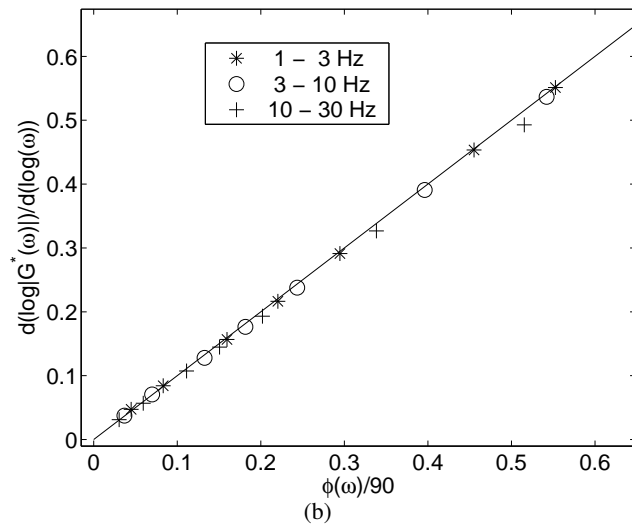
Mixture M1

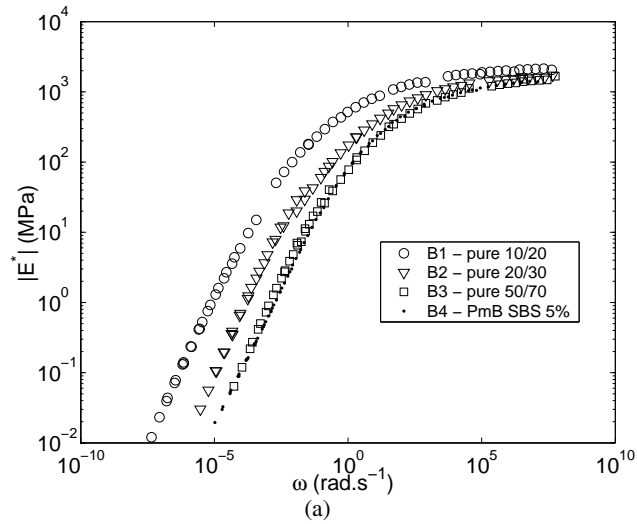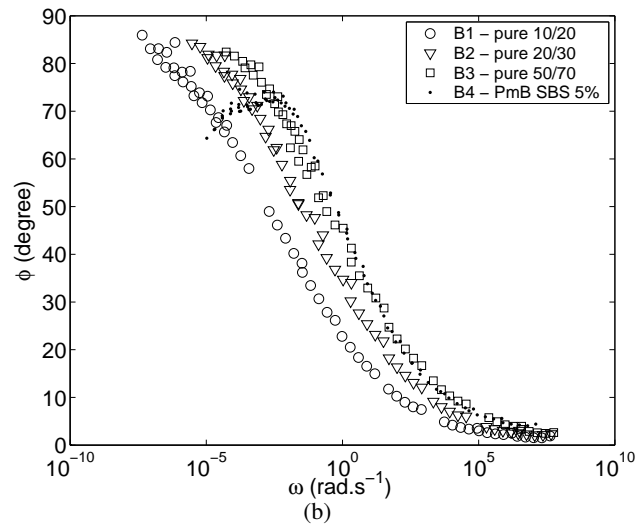**Figure 4.** *Plot of $dlog(|G^*(\omega)|)/dlog(\omega)$ according to $\delta/90$*

Black diagram

Cole-Cole curves

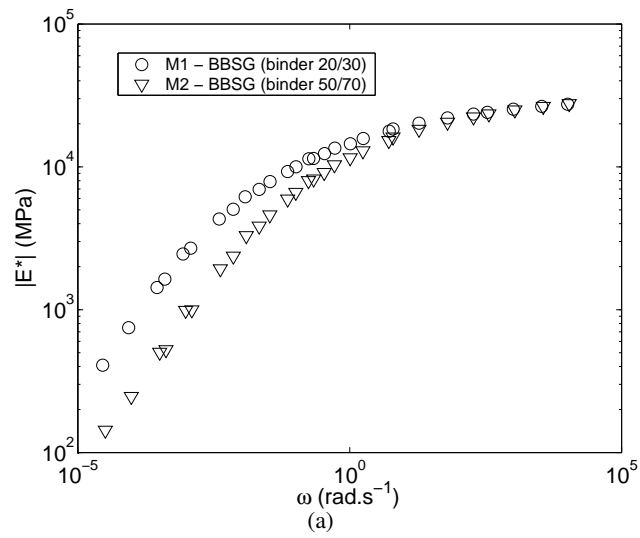**Figure 5.** *Plot of the viscoelastic measurements carried out on binders*
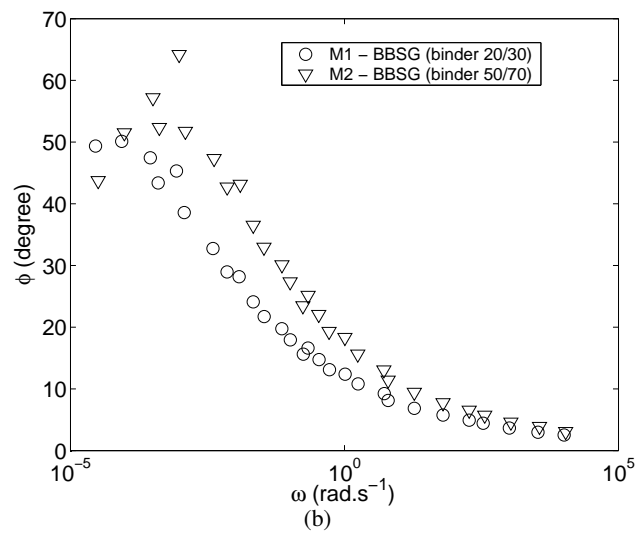
(a)

|E*| master curves

(b)

Angle master curves

Figure 6. *Master curves of B1-B2-B3-B4 binders at a reference temperature of* $0°C$

(a)

|E*| master curves

(b)

Angle master curves

Figure 7. *Master curves of M1 - M2 mixtures at a reference temperature of* $0°C$

and 7(b)) that master curves are smooth and they reflect the penetration grade of the binders. Only the data at high temperature (high phase angle) appears not to be smooth. Indeed, we generally observe that time temperature superposition principle can not be applied in this zone for mixtures.

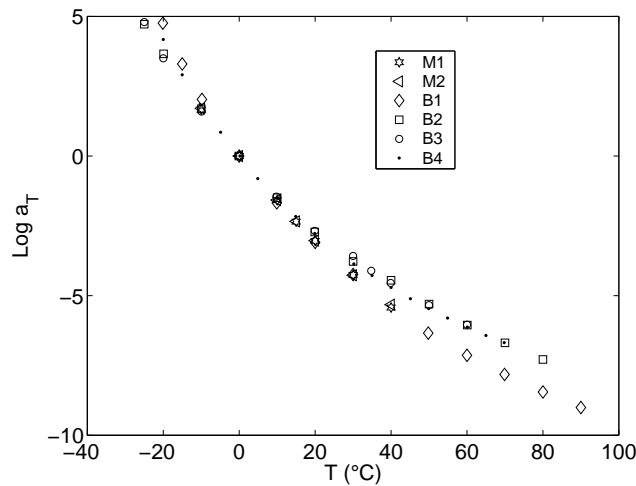### 4.4. *WLF constants analyse for binders and mixtures*

Figure 8. *Shift factors for a reference temperature of 0˚C*

Some authors have shown that shift factors of bitumen are very close to those of corresponding mixtures (Ramond *et al.*, 2003; Boutin *et al.*, 1995). Nevertheless, it was also shown that the analyse of shift factors from several bituminous materials is difficult (Olard *et al.*, 2003). Indeed, differences appear too small (see figure 8). Hence, we propose to analyse the WLF constants c_1 and c_2 which describe shift factors more precisely.

4.4.1. *Determination of the WLF constants*

Figure 9(b) depicts c_1 and c_2 according to the reference temperature. These constants are first determined by fitting the WLF law on the shift factors calculated from the relation [11] for each reference temperature (see figure 9(a)). Secondly, constants determined for the lowest reference temperature are used to calcul c_1 and c_2 at any temperature (see relations [13] and [14]). The good agreement between constants determined by the curve fitting process and by the theoretical calculus shows that WLF law is well adapted for modelling shift factors and allows to validate the procedure to construct master curve at any temperature. It has to be noted that this method can be used to detect errors from measurements.
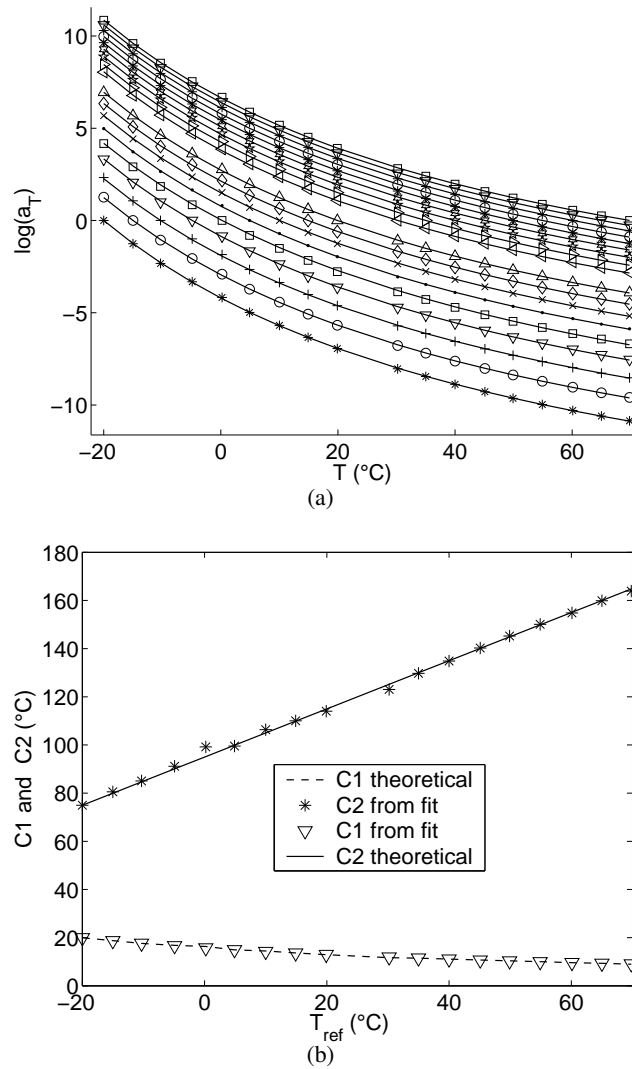
Figure 9. *(a) Systematic fit of the WLF law on shift factors determined at several reference temperatures. (b) c_1 and c_2, according to the reference temperature, determined for the binder B4*

Figure 10 shows on the same graph c_2 according to the reference temperature for non aged binders B1, B2, B3, B4 and for bituminous mixtures M1 and M2. The mixtures and non-aged bitumens appear to be separated into two groups. Value of c_2^0 for the mixtures is around 160°C and around 110°C for non-aged bitumens. It has to be pointed out that c_2 does not rank bitumens according to the penetration grade.
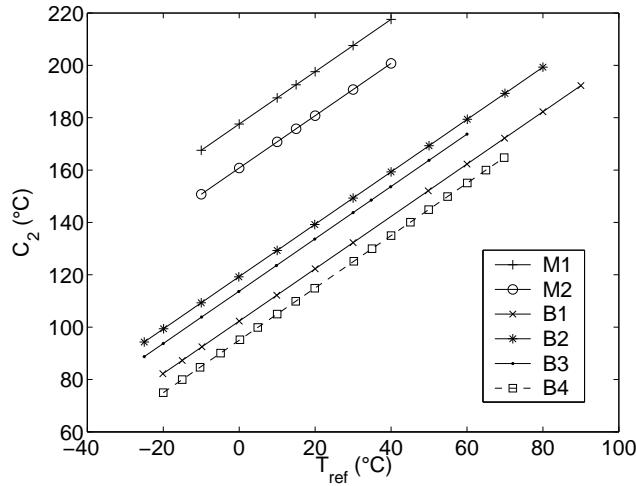

Figure 10. c_2 *constant for unaged bitumens and mixtures*

4.4.2. *First attempt to link WLF constants to physico-chemical state of bituminous materials*

It could be interesting to understand how these constants could reflect the physico-chemical state of the materials. An explanation could be proposed considering that $loga_T$ represents the gap between two temperatures. And, the more distant isotherms are, the more thermo-dependent materials are. Hence, when c_2 increases, $loga_T$ decreases (when c_1 is much more constant than c_2, which is true for bitumen B2 and B3, see table 3) and consequently shows a decrease of thermal dependence. On the other hand, ageing of bitumen leads to a widening of the relaxation times spectrum and therefore to a decrease of the thermal dependence (Chambard *et al.*, 2005). So ageing could be detected with c_2 increase as soon as c_1 allows a decrease of $loga_T$.

On the figure 11, c_2 for aged (RTFOT) bitumens B2 and B3 are plotted with the c_2 for non-aged bitumens B2, B3 and the mixtures M1, M2. Constant c_2 for aged bitumens are higher than c_2 for non aged bitumen. Ageing of the bitumen lead to reduce the difference between c_2 for the bitumens and for the mixtures. This phenomenon has a physical sense since binder is itself aged during the mixture manufacturing process. It could also mention that, regarding c_2, bitumen B3 would be less ageing-dependent than bitumen B2 (whereas penetration grading and ring ball temperature don't show

Table 3. c_1^0 and c_2^0 constants for aged and non-aged Bitumen B2 and B3. The 95 % confidence intervals on constant is determined from the non-linear fitting procedure

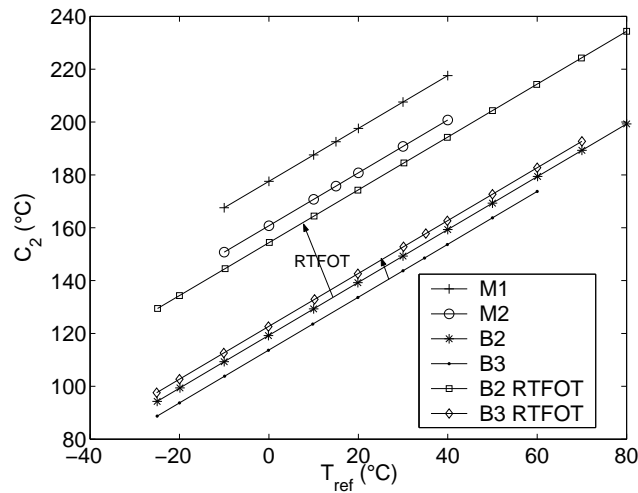| Bitumen	non-aged	aged (RTFOT)
B2	c_1^0=18.2 ($\pm$0.7)	c_1^0=22.4 ($\pm$1.6)
	c_2^0=116.1 ($\pm$6)	c_2^0=142.0 ($\pm$13)
B3	c_1^0=18.2 ($\pm$0.8)	c_1^0=20.1 ($\pm$0.8)
	c_2^0=116.5 ($\pm$6)	c_2^0=126.0 ($\pm$6)

Figure 11. c_2 constant for unaged, aged bitumens and mixtures

this behaviour). But, other parameters could influence c_2 value. More complete studies are planned in order to verify this behaviour.

Nevertheless, increase of c_2 , plotted on the figure 11, agrees with the materials ageing. We verify that $log a_T$ plotted with the WLF constants of the table 3, decrease for binder B2 and B3 on a large temperature scale (see $log a_T$ versus temperature calculated for binder B2 on figure 12).

5. Conclusion

Complex modulus, defined in linear viscoelasticity theory, meets the conditions in which ones modulus and phase angle are linked by the Kramers-Kronig relations. From a theoretical point of view, this dependence between the two parameters of the
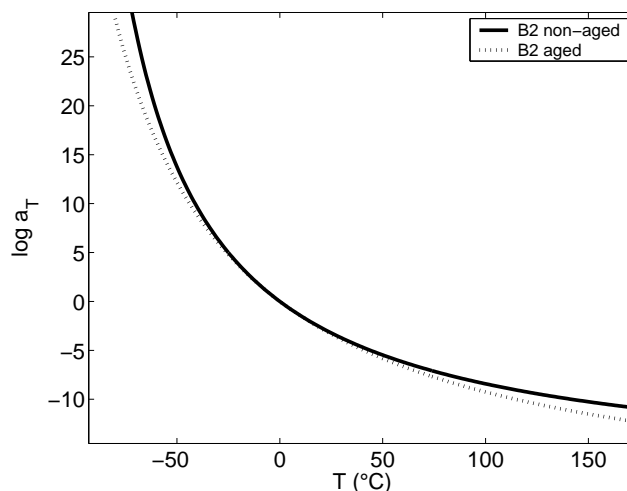
Figure 12. *$\log a_T$ calculated for non-aged and aged binder B2 with the c_1 and c_2 constants of the table 3*

complex modulus can be used to construct master curve as soon as the time temperature equivalency principle is verified.

The master curve construction method has been so formulated in detail. Verifications, from viscoelastic measurements carried out on binders and mixtures, show then that assumptions are well verified.

Master curves built with this rational method are smooth and allow to rank the binders and mixtures according to the penetration grade. The method seems interesting because it allows to adjust isotherms even if they have not some common data points.

Moreover, the WLF law, used to model the shift factors, gives possibility of constructing master curves at any temperature. In this case, relations between constants c_1 and c_2 at different reference temperatures are used.

From the WLF law, it can be pointed out that constant c_2 is linked to the thermal dependence of materials. The more c_2 increases, the less the materials is thermo-dependent. This behaviour is verified from experiments performed on non-aged, aged bitumens and mixtures. The thermo-dependence loss during ageing is pointed out by the c_2 increase.

It remains to know if the c_1 and c_2 constants could be used as parameters performance-related. Further studies will be directed in this way.

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