THIXOTROPIC BEHAVIOUR OF PAVING GRADE BITUMENS UNDER DYNAMIC SHEAR

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ABSTRACT n°0158 (182 words)

A material exhibits a thixotropic behaviour if its apparent viscosity decreases in time under stress, and if it progressively recovers its initial viscosity when the stress is released. Methods for characterizing thixotropy for fluids are relatively well known, the situation is more difficult for viscoelastic materials. For bituminous binders, it corresponds to a decrease of material stiffness under cyclic loading by modification of its internal structure and to a recovery of this stiffness after rest.

This property has been highlighted by simple shear tests, carried out using a controlled stress rheometer. An experimental procedure has been defined for studying the thixotropic behaviour of binders in dynamic mode. Then, it has allowed describing the corresponding curves of complex modulus versus the set stress and the rest period at different conditioning times of samples. This study has also permitted to demonstrate that stiffness variations are linked to re-arrangement of molecular structure and not to cracks formation and healing. Finally, based on specific indicators, it has been possible to compare different bituminous binders in order to estimate the ability of materials to restore their internal structures.

Keywords : bituminous binders, shear modulus, rheology, thixotropy, dynamic shear

1. INTRODUCTION

Roads currently undergo different damages leading to their deterioration, in particular cracking due to the fatigue of asphalt mixtures (De la Roche *et al.*, 2001). This fatigue behavior is currently assessed by laboratory tests on bituminous mixes. Fatigue tests consist in measuring the modulus loss due to a repeated application of a sinusoidal loading of constant amplitude. It is commonly admitted that the binder's nature has a strong influence on the fatigue test result (De la Roche *et al.*, 2001).

The mechanisms causing the stiffness modulus decrease during fatigue tests are not fully understood. Several explanations may be found in literature: material damaging process leading to the formation and micro and macro cracks, self heating of the material due to viscoelastic dissipation (De la Roche *et al.*, 1998) and thixotropy. All these phenomena are reversible when loading is stopped. This may be related to the stiffness recovery of bituminous mixes during fatigue tests including rest periods (Breysse *et al.*, 2002). This reversible process depends on the physical phenomenon involved: self healing in case of damage, decrease of temperature in case of self heating, and chemical links recombination in case of thixotropy. In all the above mentioned phenomena, the binder is strongly involved. This suggests that laboratory fatigue tests may be affected by artefacts (Di Benedetto *et al.*, 1996), which have to be avoided in order to obtain more relevant results.

Here we focus on bitumens known for quite a long time (Stinsky, 1975; Stefanczyk, 1993). Thixotropy has been considered as an explanation for the stiffness decrease during fatigue tests and its recovery during rest periods. Indeed these effects were observed under modes of loading followed by rest, and excluding any evaporation of light products, any temperature lowering, or any chemical phenomenon such as oxidation, condensation, or polymerization (De la Roche, 1997; Duriez and Arranbide, 1962). The usual origin of thixotropy is the breakage of the structure of the material due to mechanical or thermal constraints and its restoration after some time at rest (Barnes, 1997; Lesueur *et al.*, 1997). In contrast with healing, which develops as macro or micro cracks, thixotropy in bitumens finds its origin in the evolution of interactions (weak bonds) at a molecular or macromolecular scale.

Rheological tests, in which the stress distribution in the material is simple and controlled, appear interesting to get relevant observations concerning the thixotropic behaviour of bitumens. In this study we propose a new experimental procedure for studying binder thixotropy in cyclic mode by means of shear tests. It relies on the observation of the breakdown curves in the non-linear domain and modulus recovery curves at different conditioning times of samples.

2. DESCRIPTION OF THE EXPERIMENTAL PART

2.1 Materials

For this study, two paving grade bitumens were chosen and characterized according to different European standards: penetration test at 25°C (EN 1426: 2007), softening point (EN 1427: 2007) and asphaltene content –heptane insoluble– (NF T60-115: 2000). The results are listed in Table 1 and include the complex modulus measured at 20°C and 0.05 Hz.

These two neat bitumens were chosen because they led to very different mix fatigue performances using fatigue test EN 12697-24+A1. The fatigue performance of the mixes (thick layer asphalt concretes with a binder content of 5.4%, with the same mix design) can be found in table 1. In this table fatigue performance is expressed in terms of ε6, which correspond to the strain level leading to a life time of one million of cycles. Taking this parameter into account, bitumen Y highlights a far much better fatigue behaviour than bitumen X.

Bitumen	Penetration at 25°C (0,1 mm) (EN 1426)	Softening point (°C) (EN 1427)	Asphaltene content (heptane insoluble) (NF T60-115)	Complex modulus at 20°C and 0,05 Hz (Pa) (EN 14770)	Temperature for which $\lvert G^* \rvert \sin\delta$ = 5MPa	ε_6 (10°C, 25 Hz) (EN 12697-24+A1)
A	50	50.4	11.7	/	19.8°C	/
X	51	49.6	10.6	$1.92\ 10^5$	17.6°C	$< 100\ 10^{-6}$
Y	33	70.8	15.0	$5.30\ 10^5$	13.3°C	$> 200\ 10^{-6}$

Table 1 : Conventional characteristics of studied bitumens

The aim of the present study is to determine whether the differences in fatigue performances of the mixes can be explained by differences in binder thixotropy.

2.2 Experimental procedure for thixotropic study

The experimental procedure has been developed from previous studies (Coussot, 2005). The selected sample (bitumen A) for preliminary study devoted to the setting of the protocol was a classical 50/70 penetration grade bitumen (EN 12591: 2009). Its penetration at 25°C (EN 1426: 2007) is 50 1/10 mm and its softening point (EN 1427: 2007) is 50.4°C.

The experimental device used is a Dynamic Shear Rheometer MARS II of Thermo-Electron HAAKE trademark using a cone plate geometry (diameter of 20 mm, gap of 0.057 mm and angle of 1°) as the sensor system. This cone plate geometry was chosen in order to provide an homogeneous shear strain within the whole specimen.

The thixotropic behaviour of bitumen A is studied in dynamic mode using sinusoidal stress application, centred around zero, versus time. A relatively low frequency (0.1 Hz) has been selected to avoid inertia problems and the test temperature is set at 20°C according to a previous optimization study (Mouillet *et al.*, 2011). First, the experimental procedure consists in measuring the complex modulus in the linear viscoelastic domain. Then, a stress sweep is applied, aiming at destructuring the sample and finally the recovery, assumed to be linked to the restructuring of the sample is monitored in the linear viscoelastic domain.

The detailed experimental protocol is as follows:

❶ time sweep at very low stress (value dependent on the bitumen grade : typically 0.5 kPa) during 20 minutes to allow the sample to reach the test temperature and to measure its complex modulus in the linear viscoelastic domain (namely a modulus response independent of loading amplitude),

❷ stress sweep from 0.5 to 90 kPa (90 kPa is the maximum stress of the testing device with the chosen sensor system) to destructure the sample,

❸ time sweep at the same stress level applied in step 1 to monitor the complex modulus recovery kinetic during 3 hours.

It is worth noting that the experimental curves abscissa given in this article exhibit durations expressed in minutes. Theoretically, the second part of the curve (destructuring step) should have been plotted versus the applied stress amplitude and the third part (restructuring) versus the time because it is a kinetic curve. Nevertheless it has been decided to keep everywhere the temporal abscissa (even on the second part of the curve) in order to visualize the complete test on the same graph and make the interpretation easier.

Remark that strictly speaking the complex modulus has a clear mechanical meaning only in the linear domain. For the sake of simplicity we nevertheless chose to keep this parameter for describing the mechanical behavior of the material beyond the linear domain as it is expected that it still provides some qualitative appreciation of the evolution of the overall material stiffness in time.

2.3 Influence of conditioning time at the given temperature of 20°C before analysis of thixotropic behaviour

It is well known that bituminous binders are subjected to steric hardening (Anderson and Maresteanu, 1999; Bahia and Anderson, 1991; Brown *et al.*, 1957; Dongré, 2000; Lu and Isacsson, 2000; Traxler and Coombs, 1937; Romero *et al.*, 1999). It means that, when the material is stored at cold temperatures, it undergoes slow molecular changes making the material stiffer and less able to relax stresses. However these structural changes are reversible by simply heating the material.

The bitumen A was tested after various conditioning times (10, 90 and 300 minutes) with two repeatability trials to investigate the influence of steric hardening on the thixotropic behaviour of the sample (Fig. 1). Note that possible further understanding of the links between physical ageing and thixotropy may be obtained from systematic long duration experiments at temperatures (Ovarlez and Coussot, 2007). This will be undertaken in the future.

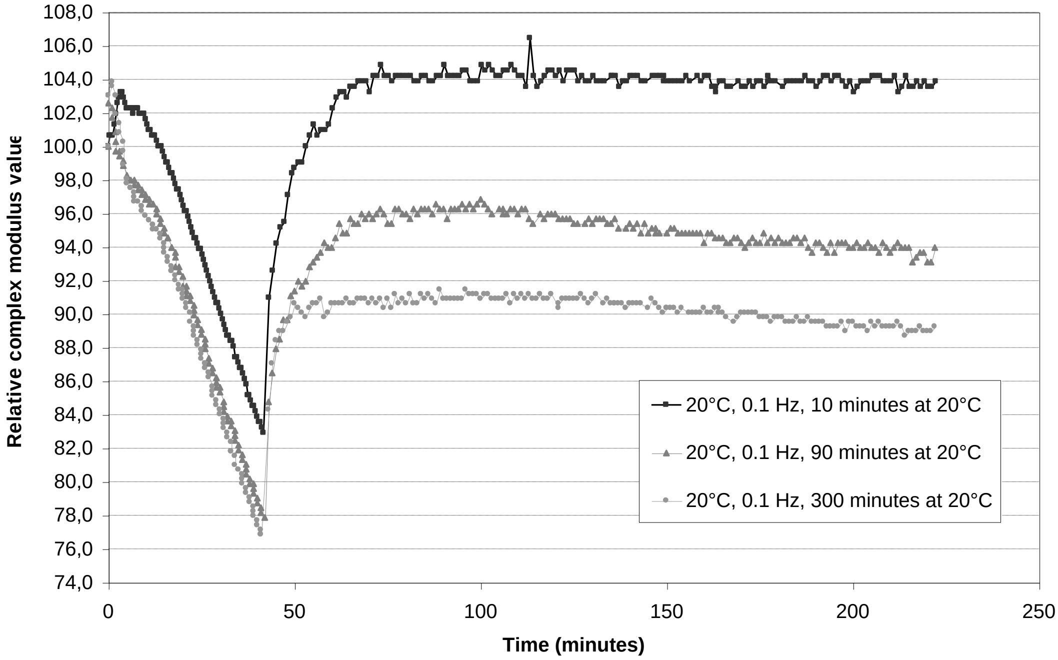

Figure 1 : Analysis of thixotropic behaviour of bitumen A within a given temperature of 20°C and a frequency of 0.1 Hz after 10, 90 and 300 minutes of 20°C temperature setting.

The first observation in relation with steric hardening is that for increasing conditioning time at 20°C, the initial complex modulus increases too. This consistency increase with time has already been observed in the literature (Brown *et al.*, 1957; Traxler and Coombs, 1937) (Table 2).

Conditioning time at the temperature of 20°C (minutes)	Initial complex modulus (Pa)	Percent of initial complex modulus at the end of destructuring step	Percent of initial complex modulus after 3 hours of restructuring
10	$3.10\ 10^5$ (γ = 0.16%)	82.9 (γ = 35.01%)	103.9 (γ = 0.16%)
90	$3.48\ 10^5$ (γ = 0.14%)	77.9 (γ = 33.19%)	94.0 (γ = 0.15%)
300	$3.63\ 10^5$ (γ = 0.14%)	76.9 (γ = 32.30%)	89.3 (γ = 0.15%)

(* Note: The results are displayed as the average of the two repeatability trials)

Table 2 : Influence of temperature set duration on the percent of initial complex modulus at the end of destructuring and restructuring steps for the measurement of bitumen A at 20°C and 0.1 Hz

Besides, when the conditioning time increases from 10 to 90 minutes, the relative value of complex modulus at the end of the destructuring step decreases from 83% to 78%. But, when the conditioning time is 300 minutes, there is no more destructuring of the sample (same percentage of initial complex modulus in comparison to 90 min conditioning time).

However, as regards to the restructuring step, the relative complex modulus reached after 3 hours of time sweep under the very low initial stress increases for decreasing conditioning time (Table 2). It can be noted that, for a 10 minutes conditioning time, the complex modulus reached after 3 hours of time sweep under the very low stress is higher than the one measured at the beginning. This is not the case for the conditioning times of 90 and 300 minutes leading to a percentage of initial complex modulus of 94 and 89% respectively and to the same strain (0.15%). It is important to note that the strain amplitude at the end of the restructuring step is the same whatever the conditioning time. Knowing that the modulus measurements during this last step have been carried out with the same stress amplitude, it means that the modulus is the same after the destructuring/restructuring process, whatever the conditioning time. Hence, this observation shows that the steric hardening phenomenon is non-only reversible by heating the material but also by loading the material under a sinusoidal stress sweep.

The best conditioning time is considered to be 90 minutes at 20°C prior to the analysis, leading to a good compromise between test duration and stability of material's stiffness.

2.4 Repeatability for measuring thixotropic behaviour

The repeatability of the testing protocol has been determined through the calculation of the coefficient of variation on 6 repeatability trials carried out on the bitumen A according to the previously chosen experimental conditions, i.e. a test temperature of 20°C, a frequency of 0.1 Hz and a conditioning time of 90 minutes.

From a quantitative point of view, the repeatability has been calculated using the relative complex modulus loss at the end of stress sweep and after the 3 hours recovery. The coefficients of variation of relative initial complex modulus at the end of destructuring step and after 3 hours of restructuring are respectively 1.9% and 1.7% (Table 3).

Repeatability tries	Initial complex modulus (Pa)	Percent of initial complex modulus at the end of destructuring step	Percent of initial complex modulus after 3 hours of restructuring
N°1	$3.48\ 10^5$	77.9	94.0
N°2	$3.61\ 10^5$	78.9	97.0
N°3	$3.76\ 10^5$	77.1	93.6
N°4	$3.88\ 10^5$	75.5	93.0
N°5	$4.14\ 10^5$	79.5	93.5
N°6	$3.88\ 10^5$	76.5	95.9
Mean	$3.79\ 10^5$	77.6	94.5
Standard deviation	$0.23\ 10^5$	1.5	1.6
Coefficient of variation	**6.1%**	**1.9%**	**1.7%**

Table 3 : Influence of temperature set duration on the percent of initial complex modulus at the end of destructuring and restructuring steps for the measurement of bitumen A at 20°C and 0.1 Hz

2.5 Identification of the bitumen's thixotropic behaviour

As already mentioned in literature (Stinsky, 1975; Stefanczyk, 1993), it is now known that the bituminous binders show a more or less strong thixotropic behaviour. However, it is important to verify that the observed phenomena are only due to thixotropic behaviour and not to physical damage (micro or macro cracks within the sample) beyond a given strain level.

So, in order to check that what is observed is linked to a thixotropic behaviour of materials, characterized as a reversible phenomenon, the bitumen A is destructured using the stress sweep defined above, from 0.5 to 90 kPa (Fig. 2). Then, the complex modulus recovery, linked to sample restructuring, is measured in linear viscoelastic mode up to 9 hours.

During the rest period, from 180 minutes to 540 minutes (9 hours), the complex modulus reaches around 98% of its initial value. As the repeatability of the percent of initial complex modulus at the end of restructuration step is around 2%, this experiment confirms the thixotropic behaviour of the material.

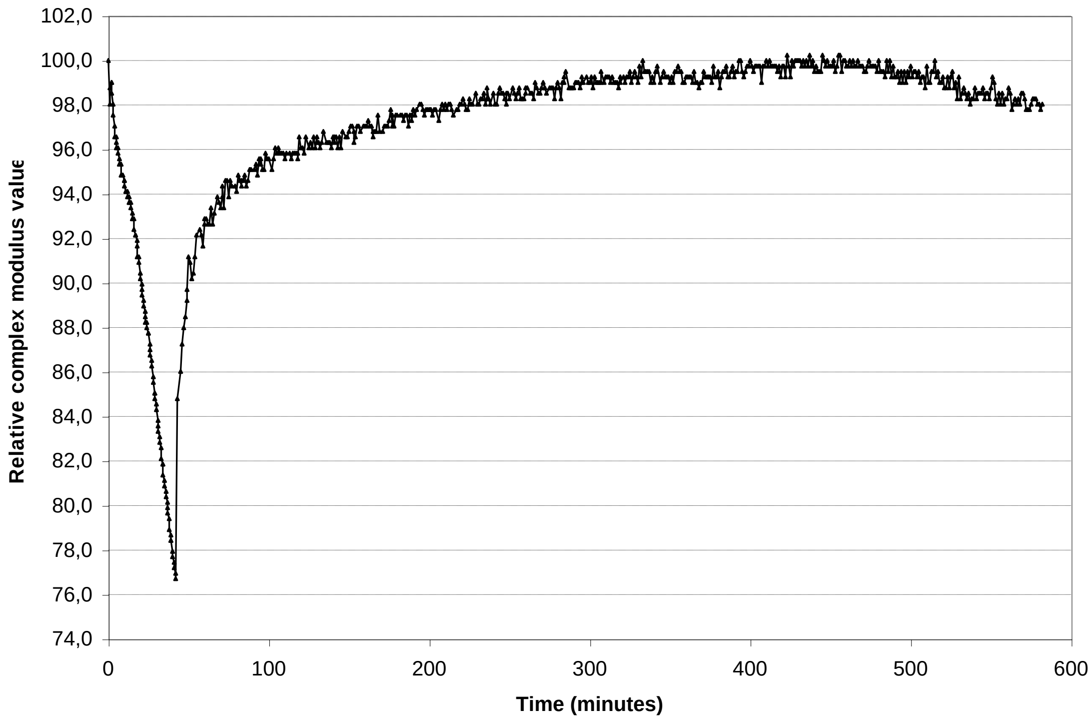

Figure 2 : Thixotropic behaviour of bitumen A (20°C, 0.1Hz and 9 hours of resting period).

3. RESULTS AND DISCUSSION

3.1 Effect of binder's nature on its thixotropic behaviour

In order to characterize the thixotropic behaviour of two road bitumens X and Y, the procedure, based on the destructuring/restructuring cycles defined above is used. Tests are performed at 20°C and at a frequency of 0.05 Hz. The frequency is lower than the previous one due to a higher complex modulus at the same temperature and frequency. The restructuring is recorded until the modulus reaches a stable value.

It has to be noted that the two bitumens X and Y do not display the same stiffness at the beginning of the test (Table 1). Nevertheless, they have been tested using the same experimental parameters (temperature, frequency), as it is done for fatigue test on mixture.

Figure 3 shows the relative values of complex modulus during destructuring/restructuring cycles performed on bitumen X and Y. With regards to bitumen X, the destructuring level of bitumen Y appears to be very important. Indeed, the complex modulus of bitumen Y reaches 45% of his initial value, whereas the complex modulus of bitumen X reaches only 80% of its initial value. The restructuring curves show also that the kinetics of recovery is faster for bitumen Y. During the first 60 min of recovery, the increase of bitumen Y complex modulus is 45%. During the same time, the recovery of bitumen X is only 10%. For those two bitumen samples, the fastest recovery is obtained for the bitumen that has the highest destructuring level.

Since bitumen Y has a very good behaviour in fatigue, it may be assumed that the fatigue performance is better for the binder that shows the most important capacity to be destructured. The reason could be as follows: during fatigue test in displacement control mode, the stress within the material decreases according to the decrease of stiffness due to the destructuring of molecular structure. Hence, the apparent loading is reduced, which implies an increase of lifetime.

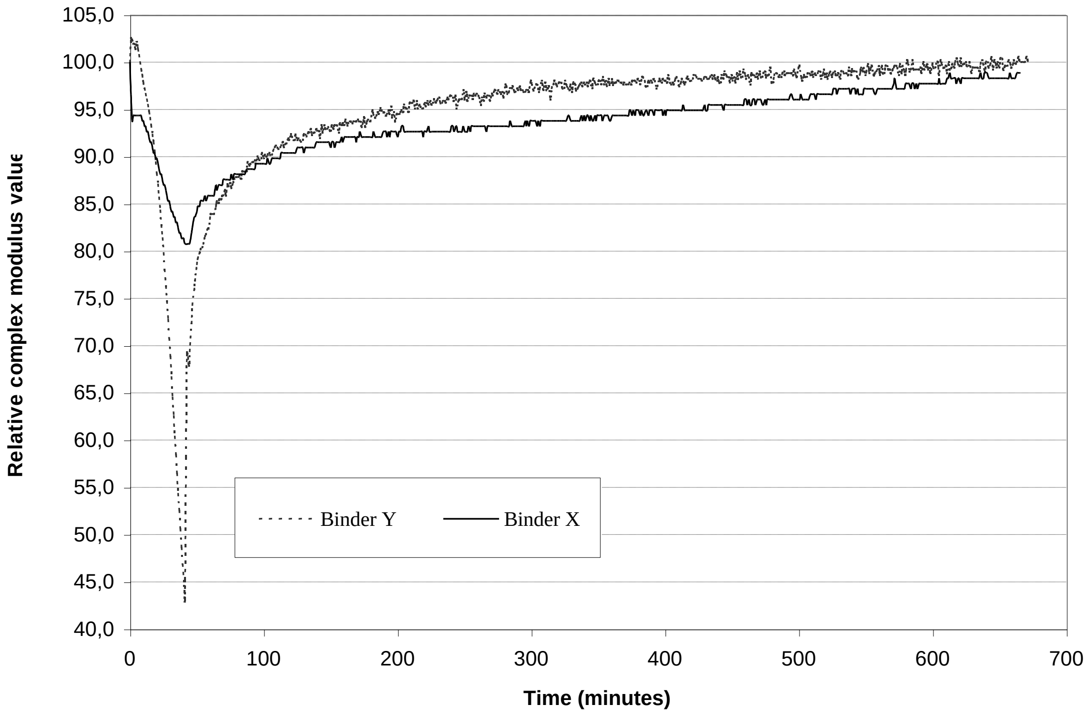

Figure 3 : Thixotropic behaviour of bitumens X and Y (20°C, 0.05Hz and 9 hours of resting period)

3.2 Effect of cycles of destructuration/restructuration

3.2.1 Study of bitumen X

At the temperature of 20°C and a frequency of 0.05 Hz, the bitumen X has been analysed during 3 identical and consecutive cycles of destructuration/restructuration steps (Fig. 4) with two repeatability trials. The obtained curve (in gray in Fig. 4) has been compared to the one of a destructuration step followed by a long enough resting period (in black in Fig. 4).

Based on the repeatability value of the restructuration step, namely 1.7%, one can say that the complex modulus values obtained after a resting period or after 3 cycles of destrcutration/restructuration cycles are identical. It means that the restructuration steps are due to a physical phenomenon, namely a reorganization of structures.

After each consecutive cycle of destructuration/restructuration steps, the destructuration level is less important and the percent of initial modulus restored after 3 hours of restructuration increases (Table 4). The bitumen X seems to be more capable of restoring its internal structure after each applied cycle of destructuration/restructuration steps.

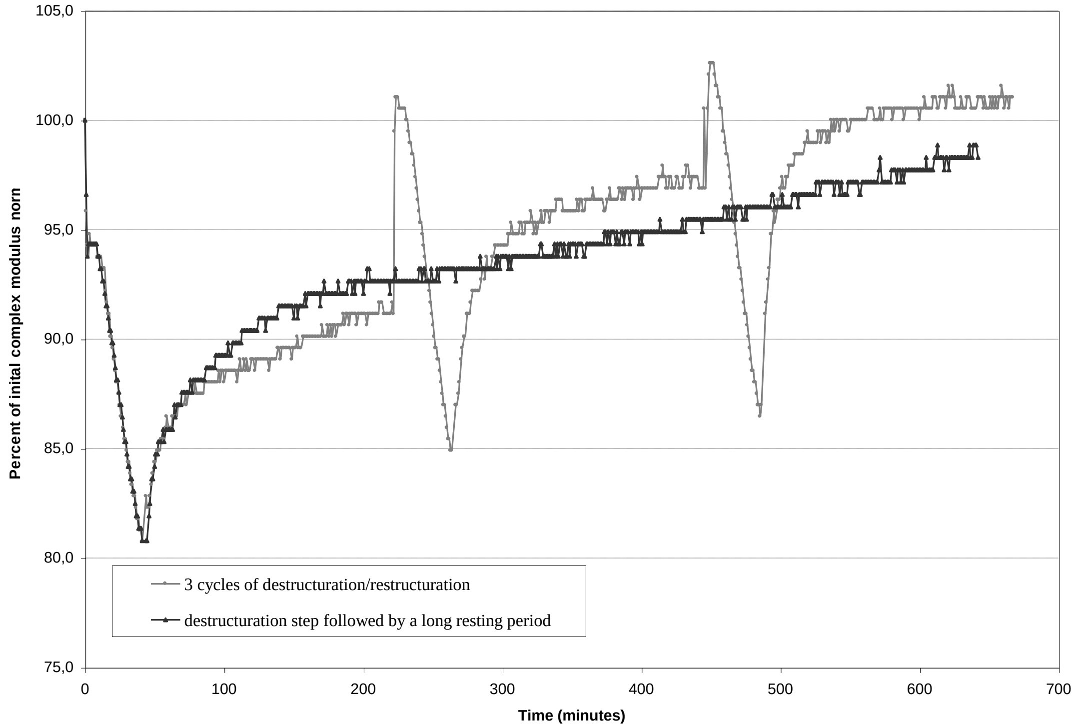

Figure 4 : Cycles of destructuration/restructuration of bitumen X compared to a single destructuration step followed by a long enough resting period

Cycles of destructuration / restructuration steps	% of initial modulus at the end of destructuration step	% of initial modulus after 3 hours of restructuration
N°1	80.7	91.1
N°2	84.9	96.9
N°3	87.0	101.0

(* Note: The results are displayed as the average of the two repeatability trials)

Table 4 : Percent of bitumen X restructuration at 20°C temperature and 0.05 Hz frequency after 3 cycles of destructuration/restructuration step

3.2.2 Study of bitumen Y

In the same manner as for bitumen X, the behaviour of bitumen Y has been analysed during three identical cycles of destructration/restructuration steps at 20°C temperature and 0.05 Hz frequency (Fig. 5) with 2 repeatability trials. As previously shown, the obtained curve (in gray in Fig. 5) has been compared to the one of a destructuration step followed by a long enough resting period (in black in Fig. 5).

Based on the repeatability value of the restructuration step, one can say again that the complex modulus values obtained after a resting period or after 3 cycles of destrcutration/restructuration cycles are identical. It confirms that the restructuration steps are due to a physical phenomenon, namely a reorganization of structures.

Unlike behaviour of bitumen X, after each cycle of destructuration/restructuration steps, the evolution of bitumen Y, namely loss of modulus at the end of destructuration step, is significantly more important (Table 5). However the complex modulus return kinetics during 3 hours are the same for each cycle of destructuration/restructuration steps. The bitumen Y acts as if it is capable to restore almost 100% of initial stiffness after each cycle of destructuration in spite of the fact of being more and more destructured.

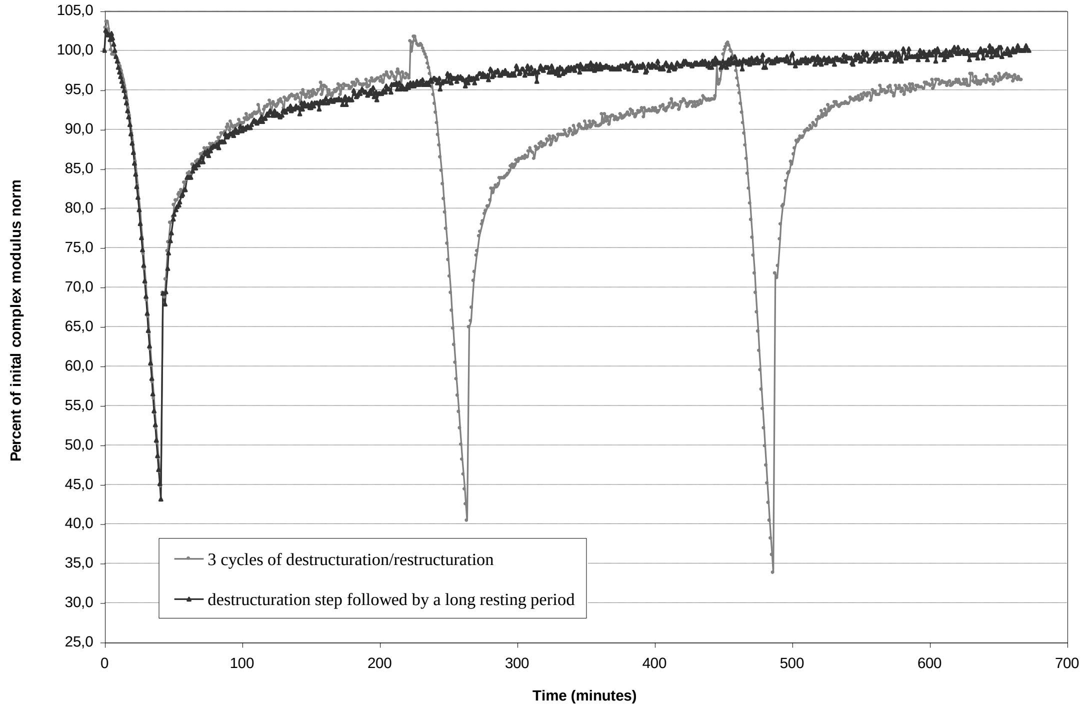

Figure 5 : Cycles of destructuration/restructuration of bitumen Y compared to a single destructuration step followed by a long enough resting period

Cycles of destructuration / restructuration steps	% of initial modulus at the end of destructuration step	% of initial modulus after 3 hours of restructuration
N°1	44.7	96.4
N°2	40.4	94.2
N°3	33.8	96.2

(* Note: The results are displayed as the average of the two repeatability trials)

Table 5 : Percent of bitumen Y restructuration at 20°C temperature and 0.05 Hz frequency after 3 cycles of destructuration/restructuration step

3.2.3 Discussion

At the end of the first destructuration step, the bitumen Y complex modulus decreases until 45% of its initial value while the bitumen X reaches 81% of its initial value. However, as the maximum linear stress values to obtain a fall of 15% of initial modulus are significantly different (49.8 kPa for the bitumen Y and 62.6 kPa for the bitumen X), the destructuration level under shear cannot be compared. Moreover, the restructuration kinetics for this first cycle are quite difficult to compare because of the different initial levels of destructuration.

However the repetition of three cycles permits one to determine the capability of the materials to restore the internal structure after different stress applications. The origin of this behaviour lies in existence of structures close to asphaltenes (Lesueur *et al.*, 1997), cancelling each other by mechanical or thermal stirring and forming up again when resting (Barnes, 1997). Consequently, the destructuration of the sample at a given shear gradient and the restructuration of the sample in linear viscoelastic region would imply the knowledge of organization and orientation of the structure's entities, as well as the rearrangement kinetic.

For the bitumen X, it seems that the repetition of destructuration/restructuration cycles leads the material to restore a little more its internal structure after each applied cycle of destructuration/restructuration steps. Moreover, the material is less destructured after each cycle, meaning maybe a better reorganization of the structures.

At the inverse, the behaviour of bitumen Y is to restore almost 100% of initial stiffness after each cycle of destructuration in spite of the fact of being more and more destructured. It acts as if the destructuration step has no influence on its behaviour.

4. CONCLUSIONS

In this study we have presented an experimental protocol which makes it possible to quickly characterize the destructuring/restructuring behaviour of road bitumens. With this protocol the influence conditioning time has been evaluated. It was shown that the observed phenomena correspond to a thixotropic behaviour of bituminous binder as they are reversible and not due to cracks formation and healing.

Our protocol also makes it possible to distinguish different thixotropic behaviour types as it was shown on bitumens X and Y that display very different fatigue behaviours of mixes. The bitumen Y showing the highest $\varepsilon 6$ in fatigue test (Table 1) appears to be more sensitive to destructuring with a faster restructuring kinetic. This suggests that there might be a link between this destructuring ability and the modulus decrease observed at the beginning of fatigue tests. Thus mix fatigue performance could be influenced by the thixotropic behaviour of binders.

This experimental procedure is simple but could be further developed in order to define, for example, an indicator of destructuring kinetic. However, the goal of this study was to show differences between materials in a simple and convenient way, using existing tools. This goal was achieved by the described experimental protocol.

5. ACKNOWLEDGEMENTS

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