Tribological and wettability study of non foaming warm mix asphalt additives at mixing and compaction temperatures

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ABSTRACT

Foaming process and additivation of bitumens are now commonly used technologies to produce Warm Mix Asphalt (WMA). However, the mechanisms of such technologies are still not well understood.
In this study, we focus on non-foaming WMA additives. A literature review shows that this kind of additives have only a slight impact on the viscosity of bitumens and allocates them lubricant and adhesion promoting properties. So they are thought to act at the surface of aggregates. In order to better understand their mechanisms during the mixing, lay down and compaction steps, both tribological and wetting experiments were conducted at high temperatures. On the one hand, friction experiments were conducted on a linear reciprocating tribometer in order to investigate the effect of additives on friction process between aggregates. In this test, a ball slides on a flat mineral aggregate immersed in hot bitumen. Both hydrodynamic and boundary lubrication conditions were investigated. On the other hand, the effects of WMA additives on the surface tension of neat bitumen were determined and the spreading of a drop of bitumen on the mineral aggregate was also investigated. Promising results indicate that organic and chemical additives don't get the same friction behaviour in boundary lubrication regime. Their contribution to surface tension is although discussed.

Keywords: Additives, Friction, Low-Temperature, Rheology, Warm Asphalt Mixture

1. INTRODUCTION

Over 100 Mt of bitumen are worldwide consumed every year, mainly for asphalt pavement applications [1]. Traditional asphalt concretes are composed of about 95 weight percent of aggregates and 5 percent of a binder, the bitumen. Because of its visco-elastic properties at room temperature, bitumen should be heated to further coat the aggregates. In practice, for a better coating, both aggregates and bitumen are heated. This mixture is classically called Hot Mix Asphalt (HMA). It is traditionally manufactured at temperatures range from 150°C to 200°C and from 100°C to 135°C during the mixing and compaction steps respectively.

According to more severe regulations and with the aims to be more competitive, to improve the safety of workers, to reduce both costs and fuel consumption and to decrease pollutant (Polycyclic Aromatics Hydrocarbons, NOx, SOx, greenhouse gas) emissions, asphalt manufacturers try to reduce the asphalt mix temperatures without (significantly) affecting the properties of the mixes. For the last twenty years, manufacturers experiment Warm Mix Asphalt (WMA) technologies whose mixing temperatures are lower, typically ranging from 100°C to 140°C.

Literature reveals the existence of many different technologies, which are now commonly used to produce WMA. Some of them are called foaming technologies and results of the presence of water in the mix. Above 100°C, this small amount of water is responsible of a global mix volume expansion which improves the mixture workability [2-4]. Presence of water results of Water Based Process or is due to foaming additives such as zeolites. Others are called non-foaming (NF) technologies. Different kinds of NF-WMA-additives are already available on the market and they do not contribute to the workability improvement in the same way: waxy components are thought to decrease the binder viscosity; others are thought to act as surface active agents [2-4].

In our work we are concerned by the question: "How do WMA non-foaming additives improve the workability of asphalt concretes?" The mechanisms by which they act are indeed currently not well understood.
Furthermore binder viscosity is a key parameter to explain the asphalt mix workability; so much that it has longtime been the only parameter into account. But it has been shown that some of the NF-WMA-additives only slightly reduce the binder viscosity and it is believed that this small reduction cannot fully explain the reduction of temperatures for producing WMA rather than HMA [5].

Recently, tribological experiments have proved that WMA are effective in improving the bitumen lubrication of contact between aggregates [5-7]. Thus lubrication is a mechanism, which can also contribute to improve the workability of asphalt concretes. In this study, we proposed to evaluate how WMA agents act on the binder viscosity, on the lubrication properties when two mineral surfaces are in contact and if they can improve the wetting properties of the binder.

2. EXPERIMENTATION

2.1 Materials

2.1.1 Bitumens

Our study is based on the addition of WMA-Additives to a 35/50 neat bitumen provided by TOTAL. Some properties of this neat binder A are summarized in Table 1.

Table 1: Penetration index and softening point of the control bitumen

Penetration	Softening Point
40 (1/10 mm)	51.4°C

Nb: Bitumen B is another neat binder which penetration index is between 20 and 30 1/10mm.

Three NF-WMA additives, chosen for their chemical properties, and bitumens references are listed in Table 2.

Table 2: Reference statement of the studied bitumens

<table>
<tr><th colspan="2">Bitumen Reference</th><th>A</th><th>Aa1</th><th>Aa3</th><th>Ab0.4</th><th>Ab1.2</th><th>Ac</th></tr>
<tr><th rowspan="3">Additive</th><th>Name</th><td>-</td><td>Additive a</td><td>Additive a</td><td>Additive b</td><td>Additive b</td><td>Additive c</td></tr>
<tr><th>Content</th><td>-</td><td>1% (wt)</td><td>3% (wt)</td><td>0.4% (wt)</td><td>1.2% (wt)</td><td>3% (wt)</td></tr>
<tr><th>Type</th><td></td><td>Surfactant</td><td>Surfactant</td><td>Surfactant</td><td>Surfactant</td><td>Wax</td></tr>
</table>

2.1.2 Aggregates

Asphalt mixes are made of aggregates of various sizes, shapes, roughness, chemical compositions etc. Unfortunately it is complex to perform both tribological and wetting studies with such rough aggregates. That is the reason why we employed flat surfaces. They are more suitable from both theoretical and practical points of view. Thus, to simplify the study 6 cm x 3 cm x 0.5 cm flat samples made of limestone and granite were wrought by a marbler. Each face of the limestone and the granite samples were polished with different roughness level. More details as the chemical composition determined by an Energy Dispersive X-Ray spectroscopy (EDX) are listed in Table 3.

Table 3: Aggregates characterization

Type of aggregate	Limestone	Granite
List of elements (determined by EDX)	Ca, O, Si, Mg (and C)	Si, O, Na, Mg, Al, Ca, Fe, Ti
Compounds present	⇨ $CaCO_3$ ⇨ $CaMg(CO_3)_2$ ⇨ iron oxides	⇨ quartz : SiO_2 ⇨ Felds path : SiO_2Al2O_3(Na/K/Ca) ⇨ Mica: $Si_6Al_2O_{20}$Mg/Fe and/or $Si_6Al_2O_{20}$Al/K ⇨ Pyroxene: Si_2O_6(MgFe)
Roughness (Ra) of flat samples (nm)	90 – 150 700	150 – 200 800 - 1200

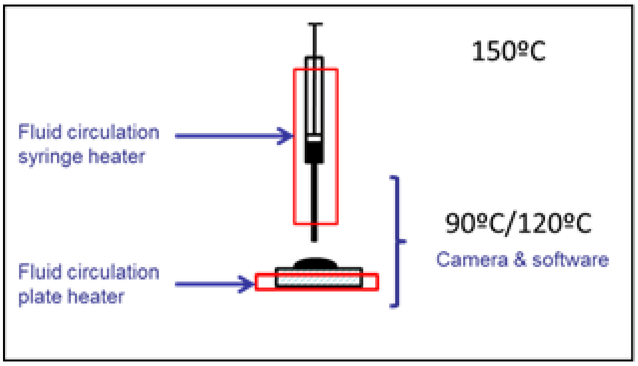
2.2 Test Methods

Bitumen viscosity measurements

A Brookfield rotational viscometer was used to determine the viscosity of virgin and WMA-modified bitumens. Viscosity was recorded at three temperatures (80°C, 100°C and 120°C) for all binders but also at 165°C in the case of virgin bitumens. Temperature was controlled by the mean of a Peltier plate.
The aim of viscosity measurements is to determine if WMA additives allow reducing mixing temperatures of warm mix asphalt.

Contact angle measurements

A Tracker tensiometer designed by Teclis Instruments has specially been modified to perform high temperature contact angle measurements (Figure 1, left). Experiments consist in laying a drop of bitumen on the mineral flat samples in air or water (Figure 1, right). A camera records the process and a dedicated-software analyzes pictures. Contact angles are then determined by fitting the shape of the bitumen drops.



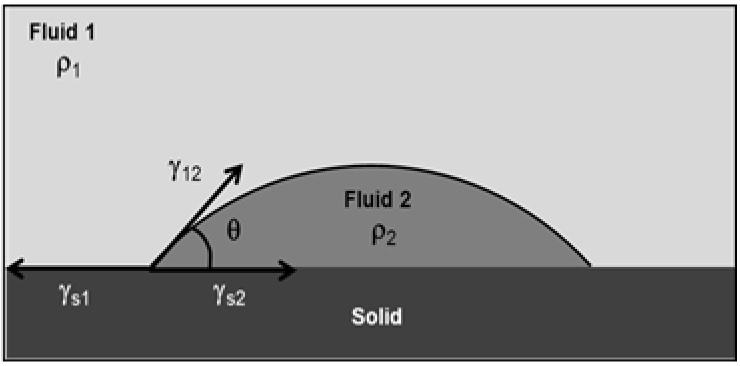


Figure 1: Scheme of the modified Tracker tensiometer (left) and contact angle definition (right)

For experiments which are carried out in water, a cell is fill with heavy water at 90°C under a nitrogen pressure of 10 bars to avoid water boiling and bubble formation. In air a fluid circulation device heats the flat plate specimens at 90°C or 120°C.

Prior to the experiments, all bitumens are heated at 180°C in an oven for 1h30 in order to pump bitumens in the syringe. Then the full bitumen syringe is clamped on the tensiometer and heated at 150°C via the oil circulation flat plate specimen heater. A minimum of five drops by flat sample are laid. Drop putting down is made manually on the roughest face of the samples.

Wetting experiments are conducted to investigate how bitumen spreads on the surface of an aggregate and if WMA-additives further improve the spreading efficiency in WMA fabrication process.

Tribological measurements

Friction tests were performed with a linear reciprocating tribometer. During a test, a Si_3N_4 ball of radius 6.35 mm slides against a mineral flat sample presented in section 2.1 (see Figure 1). Flat samples were fixed in a cup and bitumen was poured at 165°C by recovering the samples. A fifteen minutes equilibrium time was waited before beginning a test.

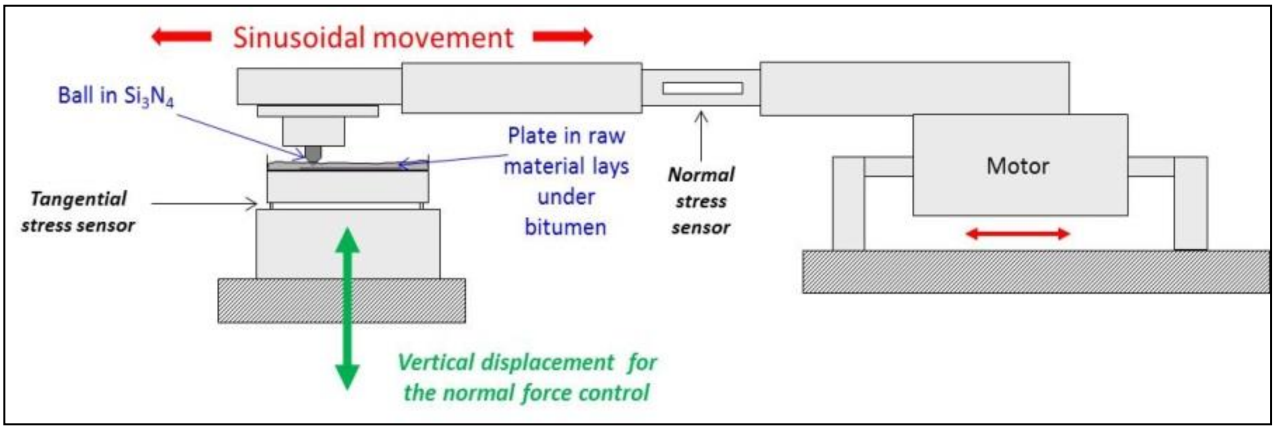


Figure 2: Scheme of the ball on flat linear reciprocating tribometer

The experimental parameters consist in sliding distance and frequency of 10mm and 0.1Hz respectively, of a 50N normal load (which creates a mean pressure of around 0.7GPa). 1600 cycles or more are generally performed during an experiment and the temperature was 120°C. Measured parameters are temperature, normal force (L), tangential force (T) and displacement. The Coefficient of Friction (COF) is then defined as COF = T/L.

Prior to the experiments, mineral plates are washed three times ten minutes in a water ultrasonic bath and dried in an oven at 100°C overnight (to remove dust contaminations). Then both ball and plates are rinsed with heptane, acetone and propan-2-ol under ultrasonic conditions. Two hours before a tribological experiment, bitumen is heated at 140°C in an oven. The friction test is performed on the smoothest face of the mineral plates.

Friction tests are performed in order to determine if bitumen does act as an inter-particle lubricant and if WMA-modified bitumens exhibits the same friction behavior as the control neat bitumen.

3. RESULTS AND DISCUSSION

3.1 Binder viscosity

As expected, Figure 3 reveals that the viscosity of bitumen significantly decreases with temperature. The linear trend visible in this figure plotted with logarithmic coordinates allows calculating an energy of activation (Ea) of 80 kJ/mol in agreement with an Arrhenius law. This value is also in agreement with common literature values of Ea for bitumen at these temperatures.

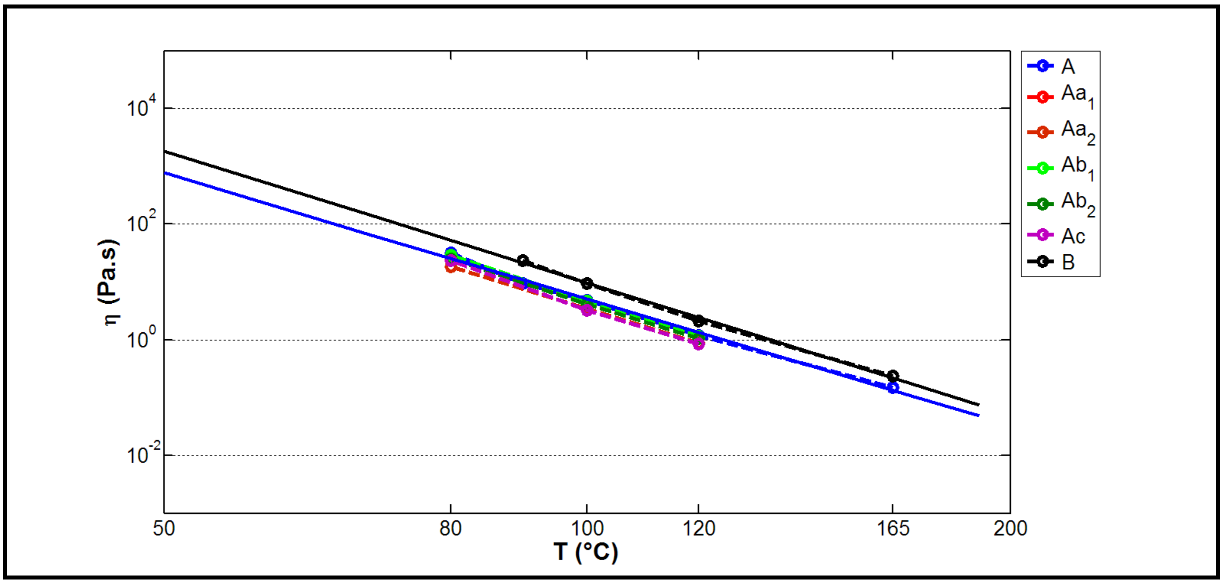


Figure 3: Evolution of bitumen viscosity as a function of temperature

For each temperature, a relative viscosity index is defined as the ratio of a WMA-modified bitumen viscosity out of the virgin binder viscosity. Figure 4 shows that WMA additives are effective in decreasing the control binder viscosity; they act as flow improvers. The efficiency for decreasing the bitumen viscosity is function of the temperature, the kind and content of the WMA-additive. However, beyond 100°C, wax components are the most effective. The most important control binder viscosity reduction is indeed obtained by adjunction of additive "c". In this case, a 27% decrease was observed. Furthermore surfactant "a" seems more efficient than surfactant "b" at all tested temperatures.

However, the control binder viscosity is reduced by 90% when temperature gets from 120°C to 160°C. As confirmed by literature review, NF-WMA agents' viscosity can therefore not fully explain the workability of WMA.

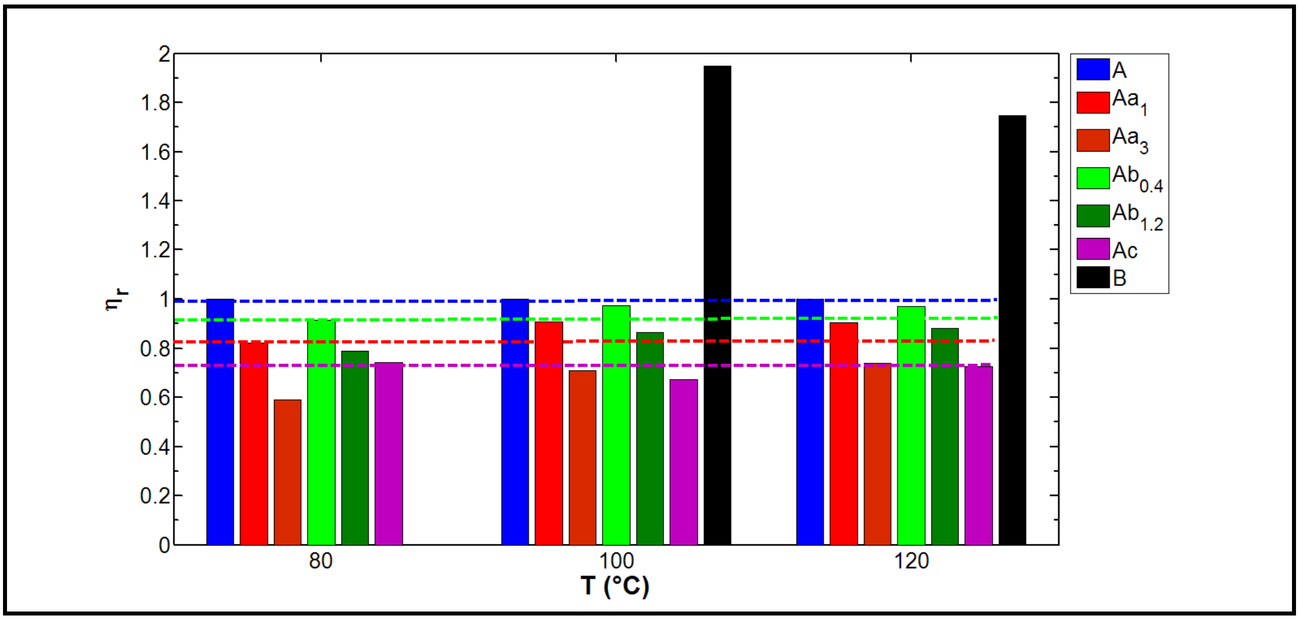


Figure 4: Relative viscosity of WMA modified bitumens.

3.2 Bitumen-Aggregate wetting study

Air environment

Thermodynamic contact angle and the time necessary to reach this steady state are usually the two sought factors in wetting experiments. In some cases, the steady state time is short but it could sometimes be very long. Moreover, in our study, the bitumen's and the sample temperatures are 150°C and 90°C respectively. That means the steady state is reached when the whole system is at 90°C and when the contact angle becomes constant. However, when the temperature drops from 150°C to 90°C, bitumen viscosity is drastically increased. This can lead to a very long equilibrium time (t_{eq}). That is why, our experiments were stopped at t = 100 s which can further be called t_{eq}.

Figure 5 shows contact angles as a function of time for several bitumens at two temperatures and different plate's material. The drop spreads out very quickly for the first seconds. According to the temperature, two behaviors are differentiated:

- If the plate is at a temperature of 120°C, the bitumen originally at 150°C spreads out very quickly (<15 s) then the contact angle remains constant.
- If the plate is at a temperature of 90°C, the bitumen originally at 150°C spreads out very quickly (<30 s) then the contact angle still decreases with time but at a much slower rate. The thermodynamic contact angle is still not reached after 100 seconds.

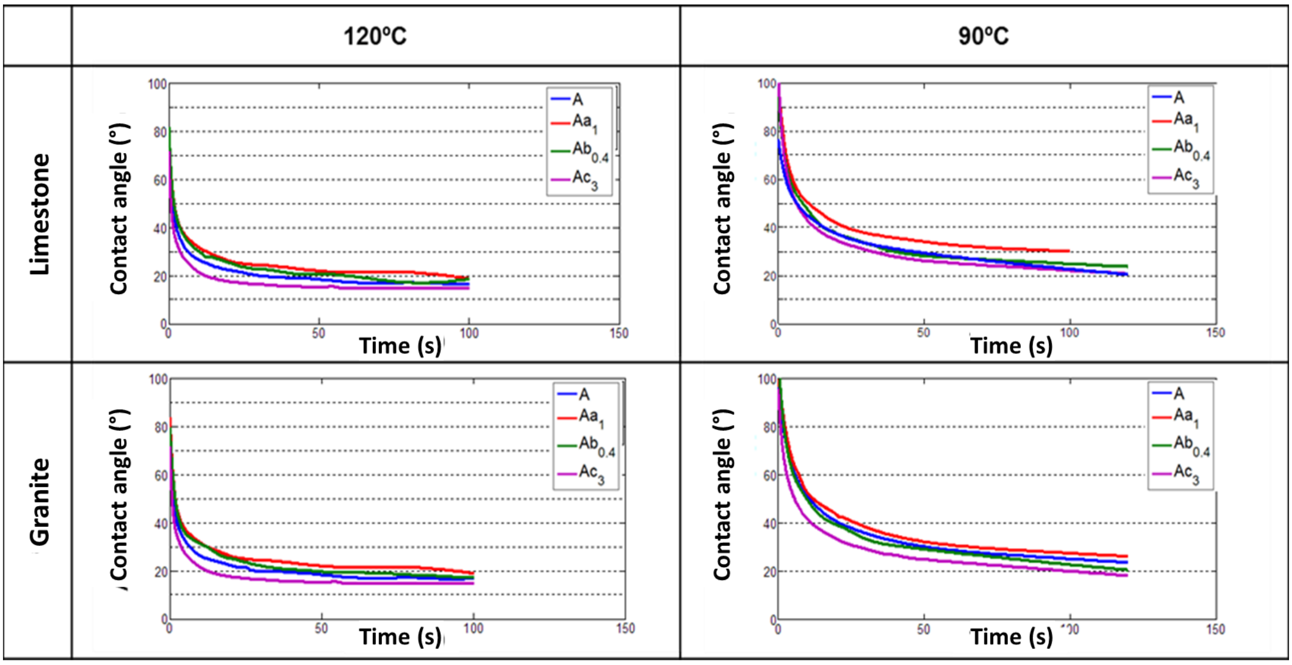


Figure 5: Evolution of the contact angle as a function of time during the spreading process of a bitumen drop laid on a flat surface

Moreover these plots show that in the case of our study, WMA-additives get the same trend with both limestone and granite plates. That is to say that bitumen "Ac" spreads out better than bitumen "A" which spreads out better than bitumen "Aa". Bitumen 'Ab' spreads out as bitumen "A" does.

<u>Water environment</u>

Figure 6 shows contact angles as a function of time for several bitumens drops laid on granite surfaces in heavy water at 90°C. In water environment, contact angles don't evolve with time: drops don't spread out on the mineral surfaces.
Moreover, contact angle values are much higher than values determined in air environment. This is due to the hydrophobic properties of bitumens (/the hydrophilic properties of water). Bitumen "Aa" gets a very low contact angle value compared to bitumens "A" and "Ac". This singular behavior reveals the surface active properties of additive "a".

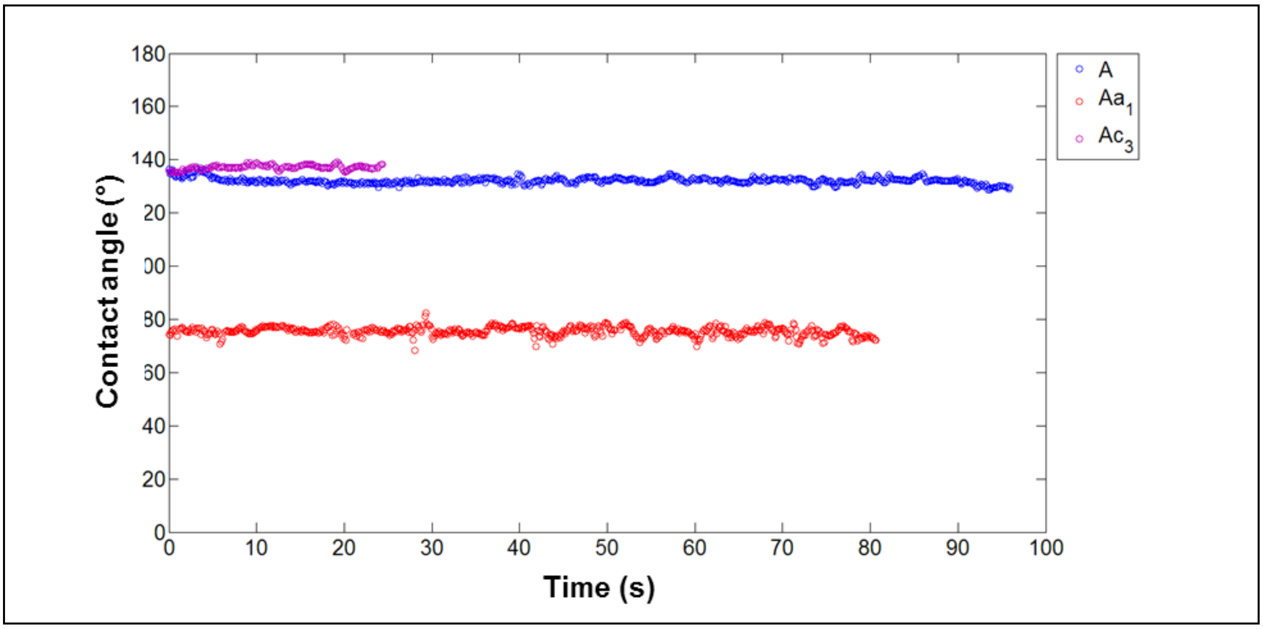


Figure 6: Contact angle measurement in water environment

We can conclude that in presence of remaining water during the mixing step of the WMA process, the additive “a” can improve the coating if aggregates are not perfectly dried.

3.3 Tribological behaviour

Figure 7 shows results from tribological experiments conducted with limestone samples at 120°C. This graph compares the mean COF of the control binder and those of the binder modified with various WMA chemical additives. Results are reproducible.

With a hot plate at a temperature of 165°C, the control binder gets an initial 0.078 COF value for the 20 first cycles. Then a sharp increase of the COF occurs. This increase corresponds to the moment were the ball and the plate comes into contact leading to wear. After 400 cycles of friction the mean COF seems decreasing. This reduction is also related to wear process: the contact area is increasing when the normal load is decreasing leading to low COF values.

At 120°C, the control binder gets an initial 0.083 COF value for the 300 first cycles. That is to say that compared with a hot sample at 165°C, more time is needed at 120°C to remove the bitumen film before the ball touches the plate. Then the COF increases up to 0.1. After that, the COF decreases and reaches a steady state with µ-values of 0.09.

Considering the WMA modified bitumens, WMA-additive “c” leads to low value of COF in the early stage ($\mu = 0.06$) and do not seem to act in the final stage where the COF is equal to the value of the control binder. It can also be noticed that wear occurs after a short initial period. This behavior suggests that this kind of components quickly move to the surface aggregate and is removed when wear occurs. One can also suppose that the initial film thickness is thinner due to the presence of wax resulting in the short wear-induction time.

Contrary to bitumen “Ac”, bitumen containing the additive “a” does not promote COF-modification in the early stage but seem to induce a COF reduction in the final stage. This reduction is related to wear process as well.

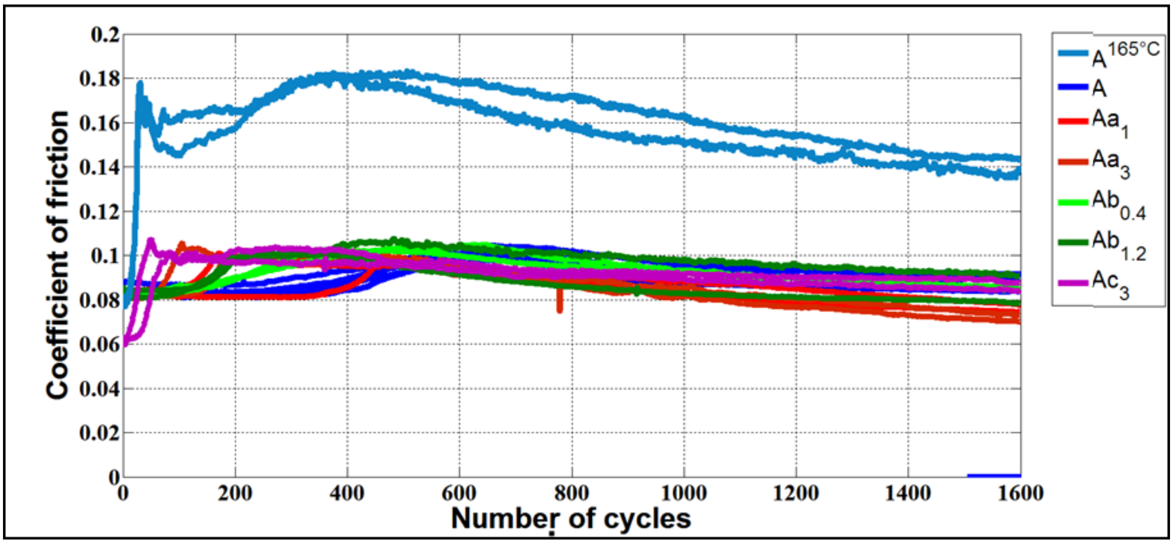


Figure 7: COF as a function of number of cycles in the case of a Si_3N_4 ball sliding against a limestone flat sample with bitumen in the contact.

When the friction tests are over, bitumen is removed by using dichloromethane. This cleaning step is necessary in order to observe wear tracks. Wear tracks volumes are then determined by optic interferometry method. Figure 8 compared the wear tracks volumes.

The maximum and the minimum wear track volumes are related to the friction test performed with the control binder and the plate at 165°C and 120°C respectively. We can also notice that WMA-modified bitumens get higher wear track volumes than the corresponding neat binder. The wear rate is (partially) linked to the duration of the initial step of friction, which is conducted in hydrodynamic lubrication range and where a viscous fluid physically separates the two sliding surfaces by hydrodynamic pressure resulting in low friction and theoretically zero wear.

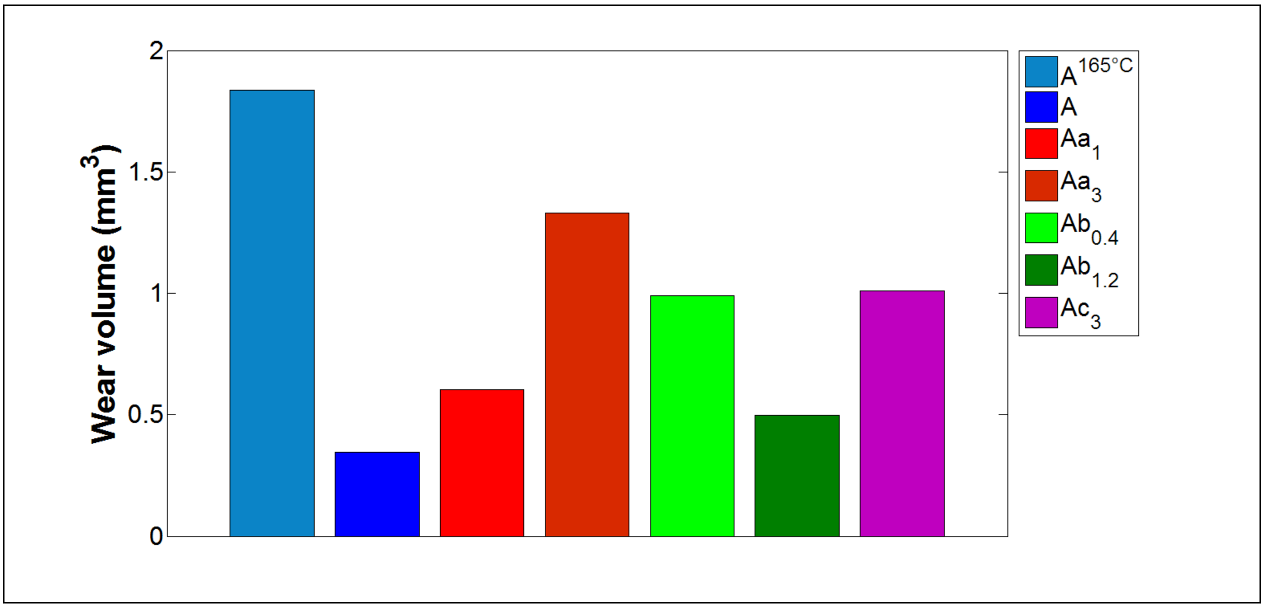


Figure 8: Wear track volumes determined after 1600 cycles of friction

4. CONCLUSIONS AND PERSPECTIVES

The viscosity study has confirmed that WMA-modified bitumens get a lower viscosity at 120°C than the control neat binder. However this decrease is negligible in front of the viscosity of the raw bitumen at 165°C.
Contact angle determination shows evidence that WMA-additives can better coat the aggregates. Results are for example strongly dependent of the WMA-additive nature and of the presence of water.
Finally, tribological investigations reveal that friction and wear are dependent of temperature and WMA-additives (type and content).

The authors keep in mind that this study is based on the WMA-modification of a single neat bitumen which cannot reflect the behavior of the large panel of bitumens. As a consequence, this study should be done again with other bitumens (e.g. more asphaltenic, acidic or paraffinic bitumens).

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REFERENCES

[1] The Asphalt Paving Industry A Global Perspective Second Edition – Production, Use, Properties And Occupational Exposure Reduction Technologies And Trends, EAPA and NAPA, 2011

[2] Pavement engineering materials: Review on the use of warm-mix asphalt, Capitão S.D., Picado-Santos L.G., Martinho F., Construction and Building Materials, 36, pp. 1016-1024, 2012.

[3] Field and Laboratory Investigation of Warm Mix Asphalt in Texas, Estakhri C., Button J., Alvarez A.E., Texas Transportation Institute, Report No FHWA/TX-10/0-5597-2, July 2010.

[4] Warm Mix Asphalt Investigation, Zaumanis M., Master of Science Thesis, 2010.

[5] Quantifying the Effects of Warm Miw Additives using the Asphalt Lubricity Test, Bahia H.U., Hanz A., Mahmoud E., Warm Mix Technical Working Group Meeting, Seattle, WA, December 16, 2009.

[6] Effect of WMA Additives on Binders Workability and Performance, Bahia H.U., Puchalski S., PMB's and WMA-binders – new experiences, NorBit seminar 2012, Grand Hotel, Oslo, October 16, 2012.

[7] Lubricity Properties of Asphalt Binders Used in Hot-Mix and Warm-Mix Asphalt Pavements, Baumgardner G.L., Reinke G.R., Brown II J., 5th Eurasphalt & Eurobitume Congress, Istanbul, June 13-15, 2012.