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WASTE FOOD WAX ADDITIVE AS A BITUMEN MODIFIER FOR WARM MIX ASPHALT PRODUCTION

Abstract

This work deals with the investigation of a waste food wax as a potentially eco-friendly modifier for bitumen binders in order to decrease the viscosity at temperatures below 120 °C. To date it is well known that — compared to classical processes — waxes lower operating temperatures of asphalt paving, thereby reducing atmospheric emissions and costs.

Hereafter we will present compare and discuss the effect of this waste wax as well as other waxy and surfactant additives on the macroscopic rheological properties by determining temperatures of viscoelastic transition and viscosities of various bitumen additives blend. Moreover we present a molecular study of the effect of the various additives by studying the molecular diffusion through the Nuclear Magnetic Resonance (NMR) diffusiometry, Differential Scanning Calorimetry (DSC) measures has been also performed on the various waxes (waste and commercial) to evaluate and compare the solid-liquid phase transition temperatures of the studied additives.

Keywords: Bitumen, Warm Mix Asphalt, Waste Food Material, Rheology, DSC, WAX.

Introduction

Bitumen is a viscoelastic multi component material generally derived from petroleum industry processes. It consists of a complex solid or semisolid colloidal dispersion of asphaltenes in a continuous oily phase of saturated paraffin, aromatics and resins [1-3]. Bitumen mechanical properties show both time and temperature dependence [4–6]. It is used as a binder for road paving by mixing it — in a percentage of about 5 % — with crushed stone materials, sand and filler. Such mixture is commonly denoted as asphalt. [7, 8]. It is very important that the selection of asphalt materials takes into account the wide variation in geographical and climatic conditions [9]. To reduce cost and emissions, nowadays different organic or chemical additives [10] — as well as modern technologies like foaming techniques — are used to enhance asphalt workability and aggregate coating by reducing bitumen viscosity or modifying its surface tension for better wettability of the aggregate, therefore reducing operation temperatures and viscosity of the asphalt conglomerate by producing what is known as Warm Mix Asphalt (WMA) [11]. It has also been proven that the reduction has a direct impact on the reduction of greenhouse gases in the atmosphere [12, 13]. This reduction of emissions is the most important reason the European asphalt industry has continuously recommended the use of Warm Mix Asphalt [14, 15].

Currently, the most common types of WMA additives generally consist of surfactants [16–19] or waxes materials able to flush the bitumen and consequentially to get better workability of the asphalt concretes at lower temperatures (100 °C — 140 °C) [20–22]. The mechanism of action of the warm mix

agent is not yet understood; some wax-based technologies seem to modify the ligand alone, while other alternative technologies — like that using surfactants — seem to act on the bitumen-aggregate interaction. This research should be considered as preliminary paper since it focuses only on the bituminous binder blended with the warm mix agents trying to find a correlation between chemico-physical parameters and the fluxing effects, by comparing the results of rheological, NMR and DSC measures of different warm mix agents. On the contrary the effect of the aggregates — that seems to be relevant in the bitumen surfactant system — will not be studied here. It will be only shown that the rheological properties of the bitumen will remain unaltered upon the inclusion of the liquid surfactant — in particular its viscosity as compared to that obtained using waxes additives — confirming that somehow aggregates plays a fundamental role in the binder surfactant system. This role will be investigated in a successive paper in which mechanical properties – like round press, Marshall, Indirect Tensile Strength (ITS) — of asphalt conglomerates obtained through bitumen-surfactant-aggregate system will also be taken into account. However, it has to be said that the invariance of rheological properties of the bitumen/surfactant system was observed only in the high temperature range, while a more significative change has been observed in the low one, in particular below minus 10 °C. This somewhat strange behaviour, necessitate more deeper investigation that is out of the goal of the present paper, but could be studied in future work on the topic. In this study, a waste wax derived from food industry — used mainly for food packaging — was tested and compared with a surfactant-based additive and — more important — with two commercial waxes. Physical chemistry characterization was performed in order to outline a possible physical mechanism induced by the bitumen modifier.

Materials and Methods

Materials

The bitumen used in this study is produced in Saudi Arabia and supplied by Lo Prete costruzioni s.r.l.. It has a 50/70 penetration grade. More details about it can be found elsewhere in Caputo et al. [23]. The other material used are:

- Sasobit (**SB**) waxes provided by Polyglass s.p.a. (solid sample);
- PE Wax (**PE**) provided by SER s.p.a. (solid sample);
- Evotherm (**WH30**) surfactant provided by Ingevity corp. (liquid sample);
- Waste Wax (**WW**) provided by KimiCal s.r.l. (solid sample).

All chemicals were used immediately after purchase.

Methods

Sample preparation

Modified bitumen samples were prepared by using a high shear mixing homogenizer (IKEA model). Bitumen was heated up to flow point at about (150 ± 5) °C and then various percentages of additive — ranging from 0.4 % to 3 % on the total mass of the bitumen — were gradually added (1 g/min) to the melted bitumen samples (100 g) under a high-speed shear mixing of 500 to 700 rpm. The mixtures have been stirred at 150 °C for 15 min to guarantee an essentially homogenous sample.

Rheological characterization

Dynamic Shear Rheological (DSR) tests on modified and on the reference virgin bitumen samples were carried out using a controlled shear stress rheometer (SR5000, Rheometric Scientific, USA) in a plate-plate geometry mode. Plate tools of ϕ = 25 mm and ϕ = 8 mm has been used for tests in the temperature range 20 °C to 110 °C and 25 °C to minus 30 °C respectively. Plate — plate gap was set to 2 mm. A Peltier system (± 0.1 °C) was used for temperature control.

Rheological responses were determined under the kinematics of both steady and oscillatory simple shears.

In steady-shear experiments, the viscosity of bitumen samples was determined from the ratio of

measured shear stress to applied shear rate, as a function of shear rate that was varied from 1 to 100 s^{-1}. Steady states were previously checked by transient experiments (step-rate test). For all samples it was observed that 10 s was a sufficient scanning time to ensure the steady state condition.

It has been found that all samples show a Newtonian behavior in the investigated shear rate range.

Dynamic tests have been carried out in conditions of linear regime where measured material features are independent of the amplitude of applied load and are function only of microstructure [24,25]. Aimed at investigating the material viscoelastic phase transition, dynamic temperature ramp tests were performed both at 1 Hz and rate of 1 °C/min in the high and low temperature range by applying the proper stress values – previously determined by stress sweep tests — to guarantee linear viscoelastic conditions at all tested temperatures.

For low temperatures measures the samples were initially kept at 25 °C for 4 mins, to obtain uniform temperature conditions, and then the test was started by cooling down from 25 °C to minus 30 °C [26].

More details about the mechanical characterization can be found elsewhere [27–30].

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was used as a convenient and reliable thermal analysis technique to analyze the characteristics of wax used in this work.

The DSC studies were performed using a SETARAM 131 instrument. The amount of each sample analyzed was around 40 — 60 mg. Analyses were performed from 25 °C to 150 °C at a temperature scan rate of 5 °C/min under nitrogen flux [31].

Nuclear Magnetic Resonance (NMR) characterization

The NMR characterization was conducted at three different temperatures (100 °C, 110 °C and 120 °C) using a Bruker 300 Spectrometer (Bruker, Italy) equipped with a Diff30 NMR probe for diffusion measurements. PFG-STE technique was used to measure molecular diffusivity [32,33]. Sixteen scans, a sequence of three π/2 rf pulses ($\pi/2$-τ_1- $\pi/2$-τ_m- $\pi/2$) and two gradient pulses δ, Δ — applied after the first and third rf pulses — has been used during the measurements. The echo was characterized when $\tau_1 = 2\tau_1 + \tau_m$ and its amplitude attenuation was derived from the Stejskal - Tanner equation:

$$I(2\tau_1 + \tau_m) = I_0 e^{-\left[\frac{\tau_m}{T_1} + \frac{3\tau_1}{T_2} + (\gamma g \delta)^2 D(\Delta - \frac{\delta}{3}\right]}, \quad (1)$$

where D represents the self-diffusion coefficient;

δ — the gradient length pulse;

Δ — the diffusion delay time g the gradient amplitude;

γ — the gyroscopic ratio of the proton nucleus and T_1 and T_2 respectively the spin-lattice and spin-spin relaxation times.

Values of 2 ms, 30 ms and 100–900 G/cm were used for δ Δ and g respectively. The NMR experiments had a very low fitting standard deviation and reproducibility of measurements. The uncertainty of D is approximately 3 %.

According to the colloidal model, two principal types of molecules constitute the general composition of bitumen on the molecular level: asphaltenes and maltenes. Asphaltenes are rigid, polar molecules and are characterized by high melting points while the maltenes on the other hand are soft, oily and they disperse the asphaltenes in the compound (bitumen). Taking into consideration the asphaltene's low T_2 relaxation times [34], the self-diffusion coefficients can be attributed to the oily part (maltene) of the bitumen. In fact, the NMR signal of the asphaltenes relaxes during the application of the pulses [35].

Results and Discussion

To start, the solid — liquid phase transitions temperatures of waxes were determined by DSC

in order to know the temperature values at which the waxes are liquid and consequently can show their fluxing effect. As it can be seen from figure 1, DSC thermogram shows that there is a huge difference in transition temperature between WW and the other (PE and SB) waxes.

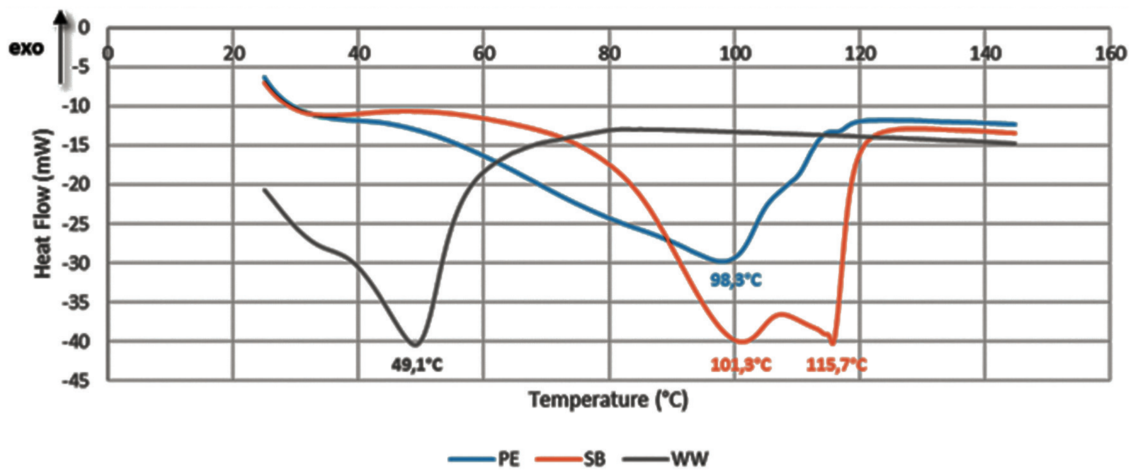


Figure 1 — Differential Scanning Calorimetry (DSC). Grey curve represents Waste food Wax (WW), blue curve represents PE wax, whlie orange curve represents Sasobit wax (SB)

In fact, the commercial waxes softens/melt in a broad interval peaked at about 100 °C and melt completely at 120 °C. On the contrary the WW shows a soften/melt interval peaked at about 49 °C, becoming completely melt at 60 °C. Moreover, SB shows 2 broad peaks centred at around 100 and 116 °C indicating the presence of two different hydrocarbon molecules, probably isomers. From these results it can be argued that the WW could have a better flow improving power under 100°C compared to the other waxes. To very this hypothesis — as we will show hereafter — we perform rheological and NMR investigations.

Table 1 shows the viscosity values obtained from DSR measurements of the virgin and modified bitumen in the temperature range from 100 °C to 140 °C.

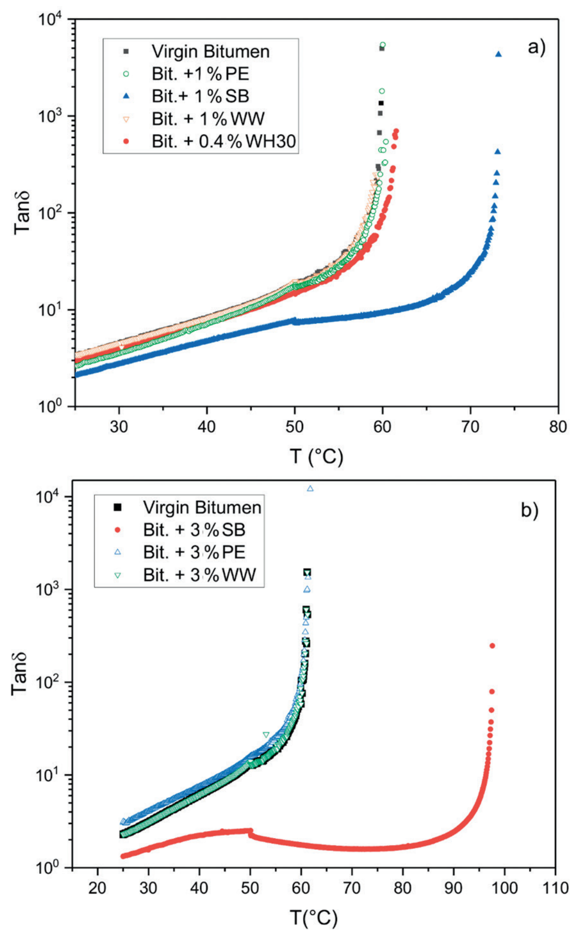
Table 1

Viscosity of bitumen with and without additives at different temperatures

Sample	Eta 100 °C (Pa-s)	Eta 110 °C (Pa-s)	Eta 120 °C (Pa-s)	Eta 130 °C (Pa-s)	Eta 140 °C (Pa-s)
Virgin Bitumen	10.3	5.3	2.8	1.4	1.3
Bit. + 0.4 % WH30	10.1	4.9	2.7	1.5	0.9
Bit. + 1 % SB	15.0	4.8	2.1	1.1	0.7
Bit+ 1 % WW	7.3	3.6	2.0	1.1	0.7
Bit. + 1 % PE	10.4	4.6	2.3	1.3	0.8
Bit. + 3 % SB	16.2	5.3	2.0	1.0	0.7
Bit+ 3 % WW	7.1	3.4	1.9		
Bit. + 3 % PE	9.8	4.6	2.5	1.4	0.8

All the viscosity data shown in table 1 are obtained by averaging data recorded in three different experiments made by the same operator. As it can be seen the viscosity of the waste food wax WW modified bitumen is significantly lower than that of the virgin one at temperature below 120 °C. It can

also be noted that SB – at both percentages studied – increases the bitumen viscosity at temperature values lower than the solid – liquid transition temperature of the additive itself. This – as could be easily guessed – is due to the presence of incompletely melted additive. As temperature increases above its melting point, viscosity values lower becoming similar to that of WW additive. PE waxes shows a similar trend. On the contrary, as expected, the liquid surfactant additive (WH30) does not significantly affect the viscosity of the virgin bitumen. In conclusion, it can be said that the additive composed of waxes derived from food scraps (WW) shows results comparable to SB and PE waxes at high temperatures but show better effects at temperatures lower than 120 °C. This can be of huge advantage in the preparation and spreading of the conglomerates at temperatures lower than 120 °C. In fact, the viscosities recorded and shown in Table 1 are always lower compared to that of virgin bitumen. Furthermore, as we will show below, this additive does not significantly change the rheological properties of the bitumen particularly in the high temperature range (25 °C — 120 °C). In fact, as it can be seen from figure 2, the only additive capable of modifying the rheological properties of the virgin bitumen is the SB wax [36] which shows — at both used percentages — a remarkable increase in the viscoelastic transition temperature (higher tan *δ*). On the contrary the other additives show very similar profiles to the virgin binder. The latter aspect however, can be seen in a positive way because an additive is often required to act only as a warm mix agent and not as a rheological modifier.



a) virgin bitumen, virgin bitumen + 1 % waxes and virgin bitumen + 0.4 % surfactant;

b) virgin bitumen and virgin bitumen + 3 % waxes

Figure 2 — Rheological properties of virgin and modified bitumen in the high temperature range

Table 2 summarizes the values of the various viscoelastic transition temperatures, the Δ*T* of viscoelastic transitions (respect to the virgin bitumen) and the percentages of the increased transition temperature.

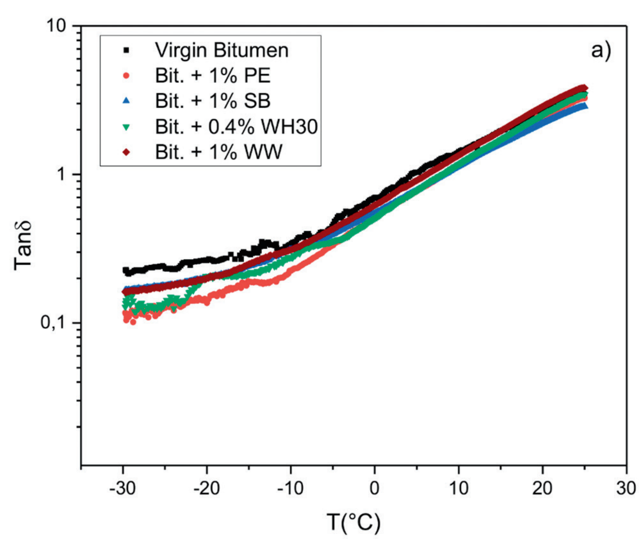
Table 2

Transition Temperatures, ΔT of viscoelastic transition and percentage of the increment of transition temperature (Ref. to virgin bitumen)

Sample	Transition Temperature (°C)	ΔT (°C)*	Increased transition temperature (%)
Virgin Bitumen	59.9	–	–
Bit. + 1 % PE	60.0	+ 0.1	+ 0.2
Bit. + 1 % SB	73.1	+ 13.2	+ 22.0
Bit. + 1 % WW	59.4	– 0.5	– 0.8
Bit. + 3 % PE	61.8	+ 1.9	+ 3.2
Bit. + 3 % SB	97.4	+ 37.5	+ 62.6
Bit. + 3 % WW	61.2	+ 1.3	+ 2.2
Bit. +0.4 % WH30	61.5	+ 1.6	+ 2.7

* Difference between the transition temperature of the modified bitumen and virgin bitumen.

From Table 2 it is evident that SB waxes lead to a significant change to the rheological properties of virgin bitumen. In particular a concentration increase leads to an increase in the transition temperatures — higher than 60 % — as compared to virgin bitumen. On the other hand, the other additives, even at concentrations of 3 %, leave these properties almost unchanged (no significantly variation from bitumen transition temperature is observed), even though they act on the viscosity of the binder. Rheological studies have also been performed at low temperature from 25 °C to minus 30 °C. The effect of various modifiers is depicted in Figures 3:



a) virgin bitumen, virgin bitumen + 1 % waxes and virgin bitumen + 0.4 % surfactant;

b) virgin bitumen and virgin bitumen + 3 % waxes

Figure 3, list 1 — Rheological properties of virgin and modified bitumen at low temperature range

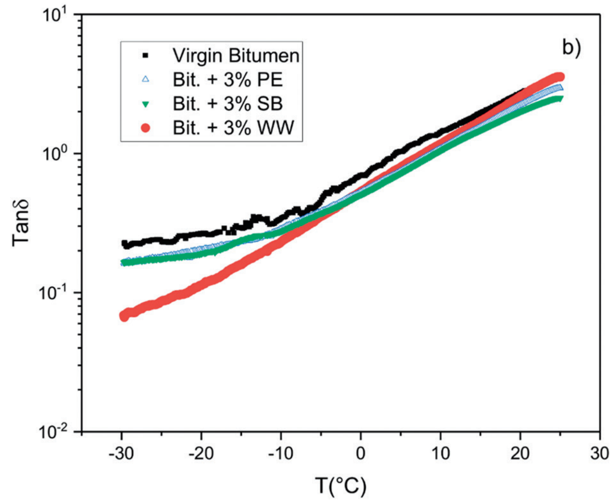


Figure 3, list 2

It is worthy to note the effect of the WW additive in the temperature range from minus 30 °C to minus 10 °C where its warm mix ability is evident particularly at 3 % w/w concentration. Tan*δ* of WW bitumen is lower than all other additives showing that the bitumen kept a good deformability of the bitumen. It seems that WW is really efficient for cold countries where the climate is more severe.

Finally, a molecular self-diffusion investigation was conducted in order to study the influence of the additives studied on the microstructural modification of bitumen. Indeed, the observation of the phenomenon of self-diffusion is based on the mobility of molecules. The motion of these molecules can be impeded due to the obstruction they face during their mobility in their media. Therefore, the SDC data, can be considered as an adequate representation of the microstructural behavior. As previously mentioned, NMR self-diffusion coefficients (SDC) give better insight into bitumen's microstructure by detecting the long-range mobility of the mixture constituents. Motion determination over long distances, in comparison with ideal micelles, facilitates a sensitive probe for the state of aggregates [33, 37]. It is important to note that the SDC values of asphaltene molecules cannot be detected due to the short transverse relaxation times (T_2) of their protons; thus, the measured SDC values are related to the maltene phase. The SDC data for each sample investigated are summarized in table 3 and represented in Figure 4 *a)* and Figure 4 *b)* respectively for 1 % (and 0.4 % of WH30) and 3 % additive added.

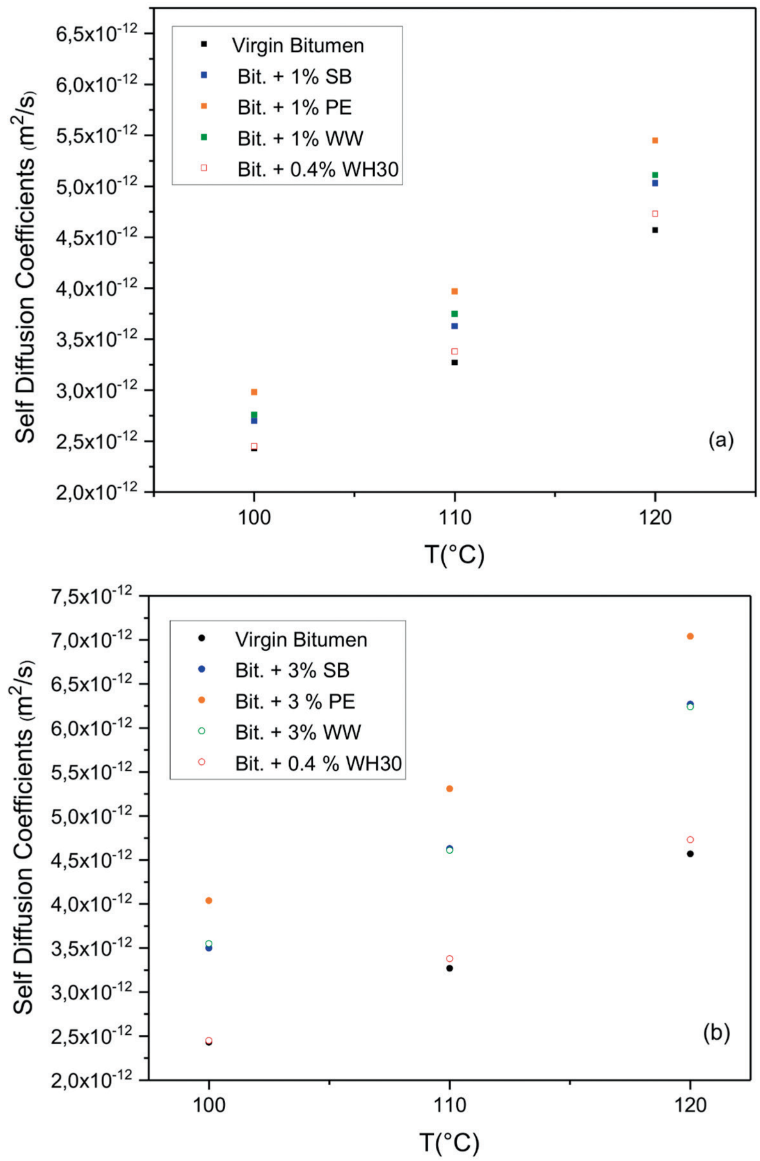
Table 3

Self Diffusion Coefficients (SDC) of virgin bitumen and modified bitumen samples at different temperatures

Sample	SDC (m^2/s) at 100 °C	SDC (m^2/s) at 110 °C	SDC (m^2/s) at 120 °C
Virgin Bitumen	2.43E-12	3.27E-12	4.57E-12
Bit. + 1 % SB	2.70E-12	3.63E-12	5.03E-12
Bit. + 1 % PE	3.72E-12	4.29E-12	5.95E-12
Bit. + 1 % WW	2.76E-12	3.75E-12	5.11E-12
Bit. + 3 % SB	3.50E-12	4.63E-12	6.27E-12
Bit. + 3 % PE	4.04E-12	5.31E-12	7.04E-12
Bit. + 3 % WW	3.55E-12	4.61E-12	6.24E-12

The end of Table 3

Sample	SDC (m^2/s) at 100 °C	SDC (m^2/s) at 110 °C	SDC (m^2/s) at 120 °C
Bit. + 0.4 % WH30	2.45E-12	3.38E-12	4.73E-12



a) 1 % w/w and 0.4 % w/w concentration;
b) 3 % w/w concentration

Figure 4 **—** NMR Self-Diffusion Coefficient in the temperature range 100–120 °C

As it can be seen from Figure 4 (*a* and *b*), the effect of the surfactant WH30 does not promote any significant improvement of the bitumen's maltene self-diffusion meaning that no particular structure modification of bitumen arises from the use of the surfactant. This support the hypotheses that the use of surfactants acts only when the biphasic system — bitumen/aggregates is taken into account. The bitumen

structure modification induced by the Sasobit and by Waste Wax is more significative than that of WH30 (at all three temperatures), and almost the same for both additives' concentrations, although at the 1 % concentration there is slightly difference between SB and WW.

On the other hand, PE shows a more marketed difference in diffusion values both with respect to virgin bitumen and SB and WW. Moreover, as it can be seen from Table 4 and Figure 5 this difference increases in the 3 % w/w concentration PE bitumen blend.

Table 4

Increased Self Diffusion Coefficients (SDC) of modified bitumen samples in comparison with virgin bitumen at different temperature

Sample	Δ SDC (m^2/s) at 100 °C	Δ SDC (m^2/s) at 110 °C	Δ SDC (m^2/s) at 120 °C
Virgin Bitumen	–	–	–
Bit. + 1 % SB	2.70E-13	3.60E-13	4.60E-13
Bit. + 1 % PE	5,50E-13	7.00E-13	8.80E-13
Bit. + 1 % WW	3.30E-13	4.80E-13	5.40E-13
Bit. + 3 % SB	1.07E-12	1.36E-12	1.70E-12
Bit. + 3 % PE	1.61E-12	2.04E-12	2.47E-12
Bit. + 3 % WW	1.12E-12	1.34E-12	1.67E-12
Bit. + 0.4 % WH30	2.00E-14	1.10E-13	1.60E-13

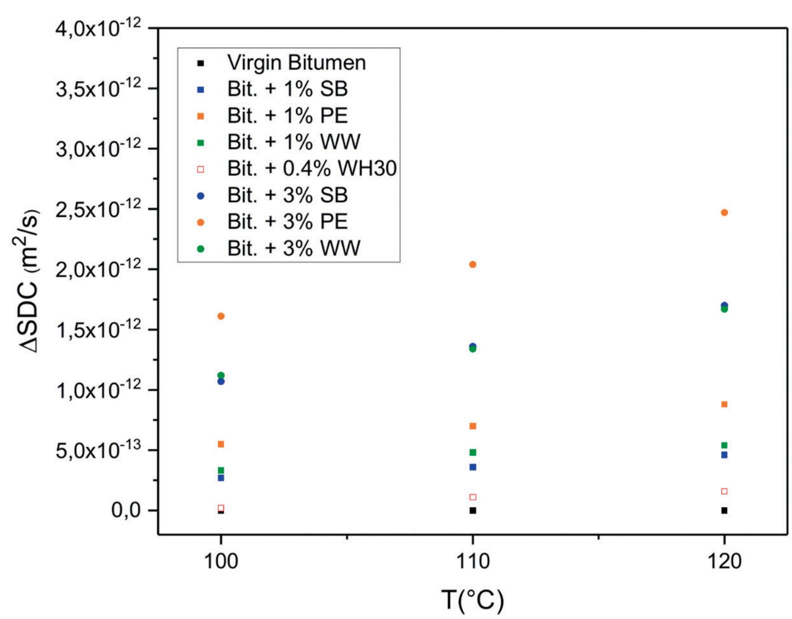


Figure 5 — Trend of the ΔSDC respect to the virgin bitumen of 1 % and 3 % waxes additives and 0.4 % of surfactant additive in the temperature range 100 °C–120 °C

The interesting point to be noted is that, although the WW is completely melted at the three temperatures tested, the molecular diffusion of the maltene phase of the WW modified bitumen is very similar to that of the SB one at all temperatures and for each concentration. In particular at 100 °C where

both SB an PE additives are partially melted, we would have expected a higher diffusion of the WW modified bitumen respect to both SB and PE. However, the higher diffusion showed by PE at 100 °C have led us to hypothesize that the molecular structure of the WW should be more cumbersome than that of PE (for example it could consist of more branched hydrocarbons unlike the linear one of PE). This hypothesis should be also valid for SB sample, because at 120 °C — where all the three waxes are melted — the PE sample shows a higher diffusion than SB one. However, this hypothesis has to be verified by a more detailed study on molecular structures of each wax, but this is not the goal of the present paper.

To conclude, it can be said that Waste Wax studied is a suitable additive to be used in warm mix asphalt production. In fact, it does not modify the bitumen rheology but decreases its viscosity at temperatures lower than 120 °C although on a molecular lever it does not enhance the maltene mobility as much as PE additive.

Conclusions

The waste wax derived from the food industry improves the workability of the conglomerate at temperatures lower than the typical operating ones. The rheological results show that these additives act only on the viscosity of the binder without changing the rheological properties of the bitumen. Their effectiveness is similar to the commercial additives currently used in road pavements. These results demonstrate that this product can be used in the asphalt industry as Warm Mix Asphalt with consequent economic savings and above all with reduction of harmful fume emissions into the environment. In fact, for Food Companies, these waxes are currently a waste, therefore transforming it into a commercial product for the road industry, they will save the cost of disposal and will also obtain earnings from its sale.

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ВІСК ХАРЧОВИХ ВІДХОДІВ ЯК МОДИФІКАТОР БІТУМУ ДЛЯ ВИРОБНИЦТВА ТЕПЛОЇ АСФАЛЬТОБЕТОННОЇ СУМІШІ

Анотація

Вступ. Наведено результати дослідження воску харчових відходів як потенційно екологічного модифікатора бітумних в'яжучих з метою зменшення в'язкості при температурі нижче 120 °С. На сьогодні добре відомо, що порівняно з класичними процесами віск знижує робочі температури асфальтобетонного покриття, зменшуючи тим самим атмосферні викиди та витрати енергоресурсів.

Мета. Встановити вплив цього воску харчових відходів, а також інших воскоподібних та поверхнево-активних добавок на макроскопічні реологічні властивості шляхом визначення температури в'язкоеластичного переходу та в'язкості різних сумішей бітумних добавок.

Результати. Представлено молекулярне дослідження впливу різних добавок на основі молекулярної дифузії за допомогою дифузіометрії ядерно-магнітного резонансу (ЯМР), вимірювання диференціальної скануючої калориметрії (ДСК). Також проводено дослідження для різних типів воску (відходи та комерційний) для оцінки та порівняння температури переходу досліджуваних добавок з твердої фази у рідку.

Висновки. Встановлено, що віск харчових відходів зменшує в'язкість бітуму за температури нагрівання менше ніж 120 °С, що дозволяє виробляти суміш за нижчих температур. Дія цього воску аналогічна комерційним воскам, які застосовують для виробництва теплих асфальтобетонних сумішей, але його вартість значно нижча, оскільки, по суті — це відходи.

Ключові слова: бітум, тепла асфальтобетонна суміш, відходи харчових матеріалів, реологія, DSC, віск.