Influence of Waxes on Polymer Modified Mastic Asphalt Performance

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1. Introduction

As a consequence of lower limit values for bitumen emissions in connection with asphalt works, and harder requirements for lower carbon dioxide emissions, new temperature reducing asphalt technologies have been developed.

One way of reducing the asphalt mixing temperature is by adding special flow improving products such as waxes. The chief purpose of adding the wax is to reduce the mixing temperature of the asphalt in order to reduce energy consumption and emissions of bitumen fumes and aerosol. As a rule, the workability of the asphalt is improved as well. Below the laying temperature, there may also be an increase in viscosity due to wax crystallization, and by that some stiffening effect. Consequently, the asphalt pavement may gain better resistance to plastic deformation. In the case of asphalt concrete, lower void content due to better compaction properties may make the pavement more durable. However, other pavement properties such as crack susceptibility at low temperatures, fatigue resistance and adhesion properties may also be affected by the flow improver. Different bitumen compositions are more or less sensitive to wax additives. Bitumen of different origin ought to be specially studied, in order to at least adjust the flow improver to the bitumen and avoiding deterioration of bitumen properties as a result of adding the flow improver.

Particularly suitable products for addition of flow improvers are hard polymer modified bitumen products. Mastic asphalt products require high working temperatures, and the use of wax additives therefore has become more frequently used, especially in Germany.

For bridges and parking decks in Sweden, mainly mastic asphalt is used. As a rule, the mastic asphalt is polymer modified and the laying temperature is about 200°C.

This paper focuses on the addition of wax to polymer modified bitumen intended for use in mastic asphalt pavements. A short introduction and background concerning wax and wax additives in bitumen and asphalt mixtures is given in the following chapters. Results from a recently initiated joint Swedish project about wax additive in polymer modified bitumen for mastic asphalt is presented.

2. Natural wax in bitumen

The influence of natural wax in bitumen and asphalt concrete has been discussed within the asphalt industry for a long time, implying negative as well as positive effects. However, natural wax in straight run bitumen today, normally is low in content and of a kind not likely to be harmful to binder properties. In other words, natural wax in bitumen is not likely to increase for instance the sensitivity to plastic deformation or cracking of a pavement. On the other hand, wax could unintentionally be produced through certain refining procedures. [Edwards 2005].

Blown (oxidized) and/or wax modified bitumens are used for road pavements in the US and Canada in order to more easily fulfil the Superpave binder specifications (according to the

Strategic Highway Research Program, SHRP). Problems due to blown bitumen and wax additives have been reported from studies in Canada [Hesp 2004].

There is some variation of opinions concerning the definition of wax and the influence of natural bitumen wax on bitumen and asphalt properties. One reason for this is the fact that different laboratory test methods give different results, for quantity as well as quality. With that, the definition of wax becomes method-dependant.

There are several test methods for determining wax content, but the most frequently used according to recent literature is determination by DSC (Differential Scanning Calorimetry). The method gives information about the total amount of wax in the bitumen. The wax content, or the crystallizing fraction, is the amount of material included in the phase transition within a given temperature range. The changes in enthalpy (heat content) are measured during a cooling and heating cycle, respectively, for the determination and calculation of the amount of crystallizing and melting material.

Waxes in bitumen often are divided into two or three general groups; macrocrystalline, microcrystalline and amorphous or non-crystalline wax. The waxes have different impact on bitumen properties. The presence of macrocrystalline wax is considered most problematic as it may have a decreasing effect on viscosity or complex modulus at high temperatures, possibly making the asphalt pavement more sensitive to permanent deformation during hot summer weather.

Macrocrystalline waxes typically have about 30 carbon atoms mainly in straight hydrocarbon chains, and may crystallize in larger crystals. If the chains are longer or contain larger amounts of branched chains or alicyclic components they form smaller crystals, microcrystalline wax. If the wax contains for instance also aromatic components, crystallization becomes more difficult and the wax is characterized as amorphous. Consequently, the different types of waxes vary in molecular weight and weight distribution as well as chemical structure and rheology. For instance, the wax melting point increases with chain length and decreases with branches and rings.

3. Wax as additive in bitumen

As a rule, natural waxes in bitumen melt between about 20 and 70°C, while waxes used as flow improver melt at higher temperature (mainly depending on longer carbon chains). The crystallization range for a wax flow improver depends on the distribution of the carbon chains and varies between different products. Molecules with long carbon chains crystallize at higher temperature than molecules with shorter chains. During crystallization, crystallization heat is released.

Typical viscosity lowering products which are used for asphalt pavements are FT-paraffin, montan wax, oxidized polyethylene wax, thermoplastic resins and fatty acid amide. Molecular weight distributions of such products vary as well as their impact on asphalt concrete or mastic asphalt properties. Zeolites are another type of additive belonging to a group of hydrated aluminium silicates, which also contains potassium, calcium and sodium ions. Aspha-min is a synthetic zeolite product, which has been used successfully as flow improver in asphalt mixes since 1998 [Barthel 2001]. However, zeolites are not used in mastic asphalt.

In the literature, FT-paraffins most frequently are mentioned. Most used in practice are FT-paraffins and montan waxes. Addition of 2- 3 % wax in mastic asphalt normally have been used.

3.1 FT-paraffin

Structurally, FT-paraffin is similar to natural paraffin wax in bitumen. The difference between bitumen paraffin wax and FT-paraffin lies in the considerably longer molecules of FT-paraffin, of which n-alkanes lie in the range of 40 to 115 carbon atoms. The longer molecules result in a considerably larger melting area for the pure FT-paraffins, 65-120°C, and a congealing point of about 100°C. FT-paraffin is produced in a so-called Fischer Tropsch synthesis, where carbon monoxide is converted into higher hydrocarbons and oxygenates in catalytic hydrogenation followed by a distillation process.

The commercial product by Schümann-Sasol GmbH is called Sasobit. Variants of FT-paraffin as flow improver in bitumen are named Bitplus (C30-C100) and Genicel (fibres+Sasobit as additive directly into the mix). Further information about product properties can be found on the home page of the producer [http://www.sasolwax.com].

The viscosity lowering effect on a binder due to the addition of Sasobit may allow working temperatures to be decreased by 18 and 54°C [Hurley and Prowell 2005]. Sasobit can be combined with polymers. A special product containing Sasobit, polymer and so-called cross-linking agent (Sasolwax Link TX) has been developed.

3.2 Montan wax

Montan vax is a partly bituminized fossil ester wax which can be extracted from brown coal. It has a more complicated structure compared to FT-paraffin and is available in a number of product variants depending on range of use (type of bituminous product).

Romonta GmbH in Amsdorf is the largest producer of crude montan wax of different kinds since the twenties. Romonta Normal was the first marketed bitumen flow improver. Other similar developed products after that were named Asphaltan. Asphaltan A was developed specifically for modification of mastic asphalt products, and Asphaltan B for asphalt concrete mixtures. Further information about the products can be found on the home page of the producer [http://www.romonta.com].

Since the beginning of the 1980's, montan waxes have been used as additive for mastic asphalt, initially as a result of harder requirements for lower carbon dioxide emissions in Germany but later also for obtaining better workability of asphalt mixtures. Montan waxes have been modified specifically for this purpose, but also with the intension of improving for instance asphalt pavement adhesion properties. Romonta N, Asphaltan A and Asphaltan B have congealing points of about 78°C, 125°C and 100°C, respectively.

3.3 Influence of wax additives

The main purpose of adding wax to bitumen normally is to lower the viscosity within a certain temperature range. In turn, this may lead to better workability, perhaps a longer paving season and less needed roller compaction (for asphalt concrete mixtures).

Energy consumption reductions are considered to be a very important benefit of wax addition (and other similar techniques). Production costs at the asphalt plant may be lower due to lower production temperature and shorter production time. Less wear of equipment in the plant is another possible favourable consequence. On the other hand, production costs may increase by the extra cost of wax, and if equipment modification is needed for the new production process.

Lower production temperature also means reduced emissions, which otherwise may be a problem, or even injurious to health, during asphalt production and paving. Bitumen fume in connection with indoors. Asphalt works at areas are places are known to be most problematic.

Wax as flow improver shows a softening effect on the binder and asphalt mix at higher temperature (above 80°C). In addition to that, a stiffening effect occurs below the paving temperature as a result of wax crystallization. By that, the asphalt pavement resistance to permanent deformation may be improved as well. Rheological effects of adding wax to bitumen can be studied using dynamic mechanical analysis (DMA). In DMA, the ratio of peak stress to peak strain is defined as the complex modulus $|G^*|$, which is a measure of the overall resistance to deformation of the sample tested. The phase difference between stress and strain is defined as the phase angle δ, and is a measure of the viscoelastic character of the sample. For a completely viscous liquid, the phase angle is 90° and for an ideal elastic solid material, the phase angle is 0ot´r above or °. Complex modulus and phase angle of bitumens are functions of temperature and frequency, which may be changed by the addition of different additives such as waxes and polymers.

4 Wax additive in polymer modified bitumen for mastic asphalt – A Swedish research project

The influence of adding commercial wax to polymer modified bitumen intended for use in coarse aggregate mastic asphalt is studied in this research project. The purpose of the study is to find out if the mastic asphalt product normally used today for Swedish bridge decks, parking decks and terraces can be made more environment friendly and easier to handle by adding a suitable wax to the polymer modified binder. Wax modification is expected to lower the laying temperature and by that reduce emissions of bitumen fumes as well as carbon dioxide. However, the additive must not have any obvious negative effect on the performance of the mastic asphalt.

The project is divided into the following four parts:

1) Survey of current knowledge and experience
2) Laboratory study on binder mixtures
3) Laboratory study on mastic asphalt mixtures
4) Field trials

One polymer modified product (Pmb 32) and two commercial waxes (Sasobit and Asphaltan A) have been selected for the project. Results from the laboratory study on binder mixtures are presented in the following sections. Further laboratory testing will be performed on mastic asphalt test specimens containing selected binder mixtures.

4.1 Pilot study

In a pilot study, binder mixtures of the polymer modified bitumen product Pmb 32 and FT-paraffin Sasobit (S) were prepared. Levels of 3 and 6 %wt wax were used. Dynamic viscosity at temperatures from 100 to 200°C was determined, and DSR sweeps from 10 to 100°C performed. The results show that this wax additive has a certain viscosity reducing effect on Pmb 32 at higher temperatures, starting at about 150°C. This is shown in Figure 1. At temperatures lower than approximately 100°C, there is some stiffening effect due to the wax. This is shown in Figure 2. The complex modulus is increased and the phase angle decreased, indicating positive effect on stability.

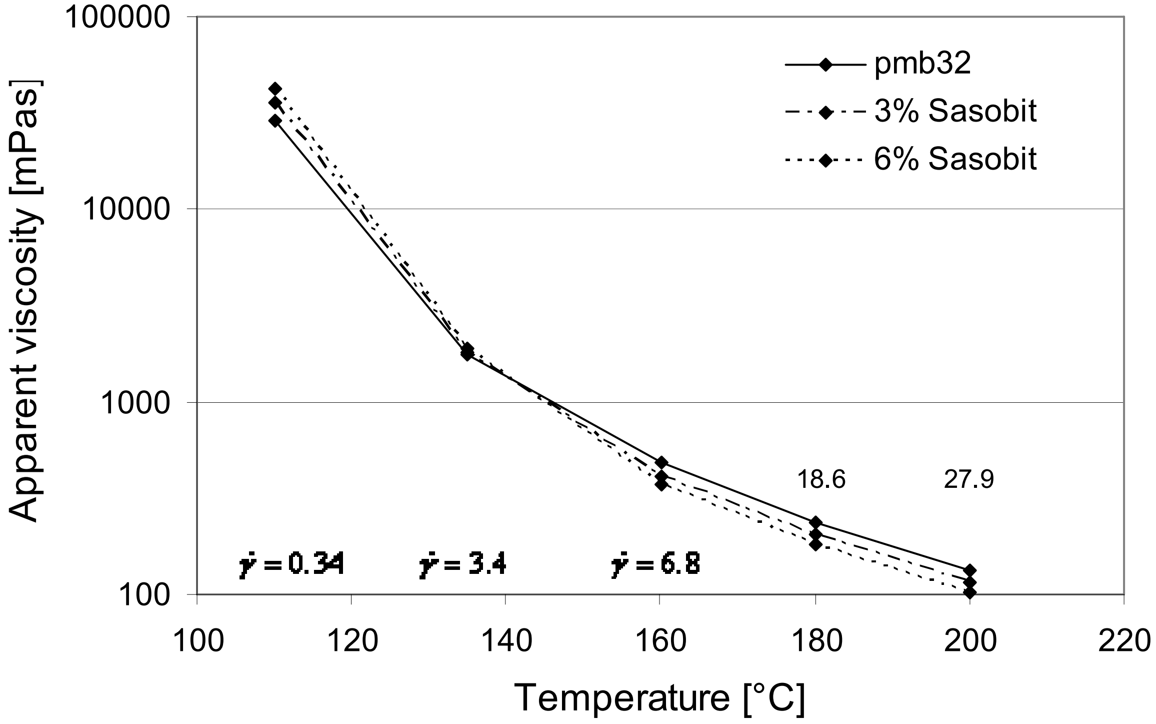

Figure 1 Viscosity measurements from 100 to 200 °C for Pmb 32 containing wax.

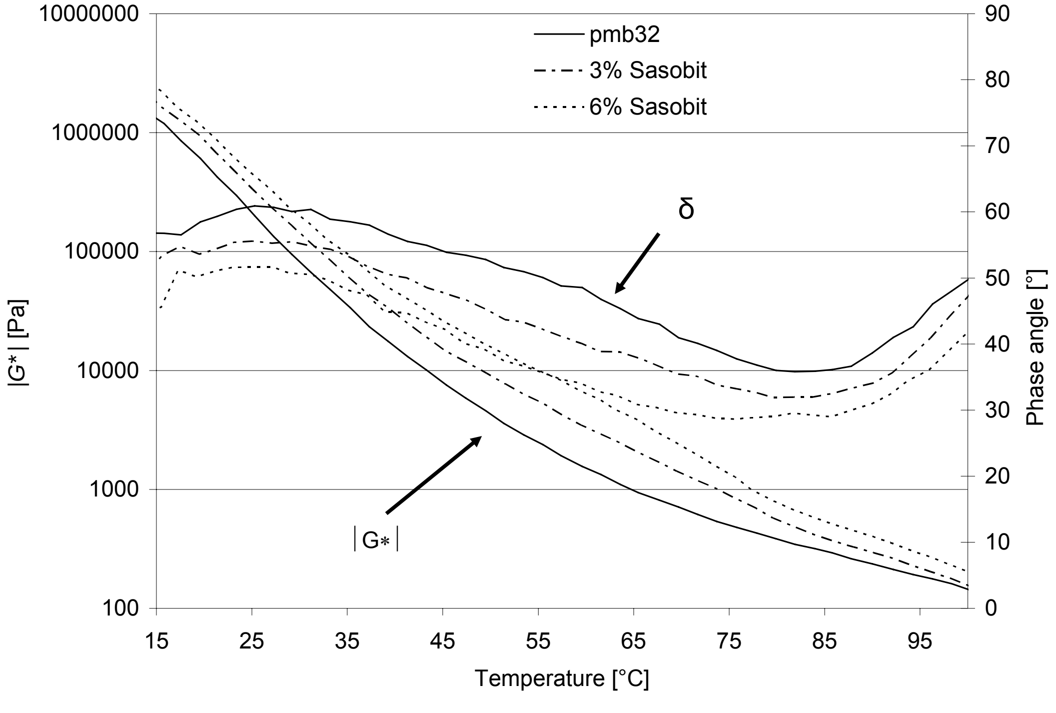

Figure 2 DSR temperature sweep from 10 to 100°C at a frequency of 1 rad/s for Pmb 32 containing wax.

4.2 Main study

In the main study, binder mixtures of the polymer modified bitumen product Pmb 32, FT-paraffin Sasobit (S) and montan wax Asphaltan A (A) were prepared. Levels of 3 and 6 %wt wax were used. Testing was performed before and after ageing in RTFO (Rolling Thin Film Oven) at 163°C. The following test methods were used:

- Softening point (EN 1427)
- Penetration at 25°C (EN 1426)
- Breaking point Fraass (EN 12593)
- Dynamic viscosity, Brookfield at 135 and180°C (ASTM D442)
- Elastic recovery at 10°C (EN 13398)
- Force ductility at 10°C (EN 13589, EN 13703)
- Storage stability at 180°C (EN 13399)

- Chemical characterization using IR and GPC
- DSR temperature sweep from -30 to +80°C at a frequency of 10 rad/s (AASHTO TP5)
- BBR analysis at -18 and -24°C (EN 14771)
- DSC (Differential Scanning Calorimetry)

Results (presented in Table 1) show a viscosity reduction of approximately 60 units at 180°C by the addition of 6% Sasobit or Asphaltan A, corresponding to a possible temperature reduction in laying temperature of about 10°C.

Adding Sasobit shows a somewhat larger stiffening effect, compared to Asphaltan A, at temperatures around 30 to 60°C. This is indicated by higher complex modulus and lower phase angle as shown for original samples in Figure 3, and laboratory aged samples in Figure 4. The influence on softening point and penetration also is larger for Sasobit compared to Asphaltan A, especially for original samples.

Storage stability seems to be improved by the addition of wax. Or rather, the softening point is increased to an extent corresponding to what also happens during laboratory ageing in RTFO. Pmb 32 with no wax is not storage stable, and the softening point is only marginally changed by laboratory ageing. Consequently, the softening point initially is increased by the addition of wax, but also further increased if stored or aged. After storage for 72 hours at 180°C, all samples containing wax show a softening point of about 100°C. After ageing, the softening point is about 90-100°C for all samples containing wax. It should be noted about Pmb 32 that the softening point may vary depending on sample preparation temperature and time. According to the bitumen producer, the sample preparation temperature must be 180°C. According to product data sheet for Pmb 32, the softening point shall be minimum 75°C. In this particular study, the sample preparation temperature was 180°C. But still, the softening point may vary depending on sample preparation time.

The elastic recovery at 10°C is somewhat decreased by the addition of 3 % wax. At the higher wax level, test specimens break before reaching the elongation length of 200 mm (as specified in the test method). After ageing, all samples containing wax break during the test.

Also in force ductility at 10°C, all aged samples containing wax break (before elongation to the specified 40 cm according to that test method). As force ductility is considered to be a measure of cohesion and homogeneity of the test sample, the test results indicate a stiffening effect at 10°C related to probably a decrease in cohesion of the sample.

Concerning low temperature performance, the breaking point is slightly affected by the addition of wax. Low temperature testing by BBR shows an overall increase in stiffness at -18°C, indicating a negative impact on crack susceptibility at low temperatures, somewhat larger by the addition of Sasobit than by the addition of Asphaltan A. On the whole, these waxes show little (or no) negative effect on the low temperature performance of Pmb 32.

Table 1 Test results for Pmb 32 with and without wax additive

Characteristic	**Pmb 32**	**Pmb +3% S**	**Pmb 32 +3% A**	**Pmb 32 +6% S**	**Pmb 32 +6% A**
Softening point, °C	74	96	70	94	77
Penetration, dmm	56	39	51	35	45
Breaking point Fraass, °C	-15	-11	-12	-10	-13
Elastic recovery 10°C, %	79	75	73	Break at 7-8 cm	Break at 15-18 cm
Force ductility 10°C, Nm	5,5	6,7	5,1	5,5	5,6
Brookfield visc. 135°C, mPas	1 636	1 419	1 150	1 192	945
Brookfield visc. 180°C, mPas	299	273	260	239	236
BBR -18°C, S MPa /m-value	225/0.319	234/0.282	214/0.318	314/0.260	212/0.296
Storage stability at 180 °C:					
Softening point top, °C	100	103	95	106	100
Softening point bottom,°C	72	93	94	101	99
After RTFOT					
Softening point, °C	70	94	88	99	90
Penetration, dmm	38	25	28	22	30
Breaking point Fraass, °C	-11	-11	-14	-7	-14
Elastic recovery 10°C, %	65	Break at 6 cm	Break at 9 cm	Break at 2 cm	
Force ductility 10°C, Nm	6,1	7,2*	7,3*	5,4*	4,6*
BBR -18°C, S MPa / m-value	239/0.304	303/0.248	294/0.275	363/0.225	299/0.278

* Break at ≥ 3 dm

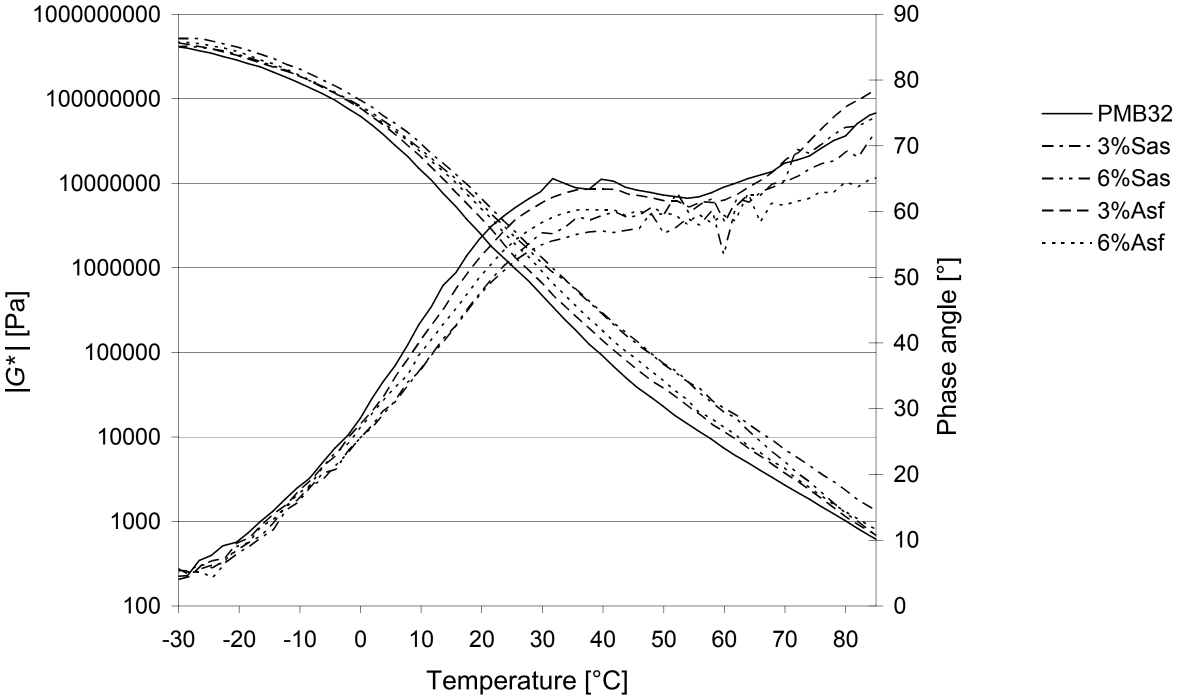

Figure 3 DSR temperature sweep from -30 to 80°C at a frequency of 10 rad/s for Pmb 32 containing wax.

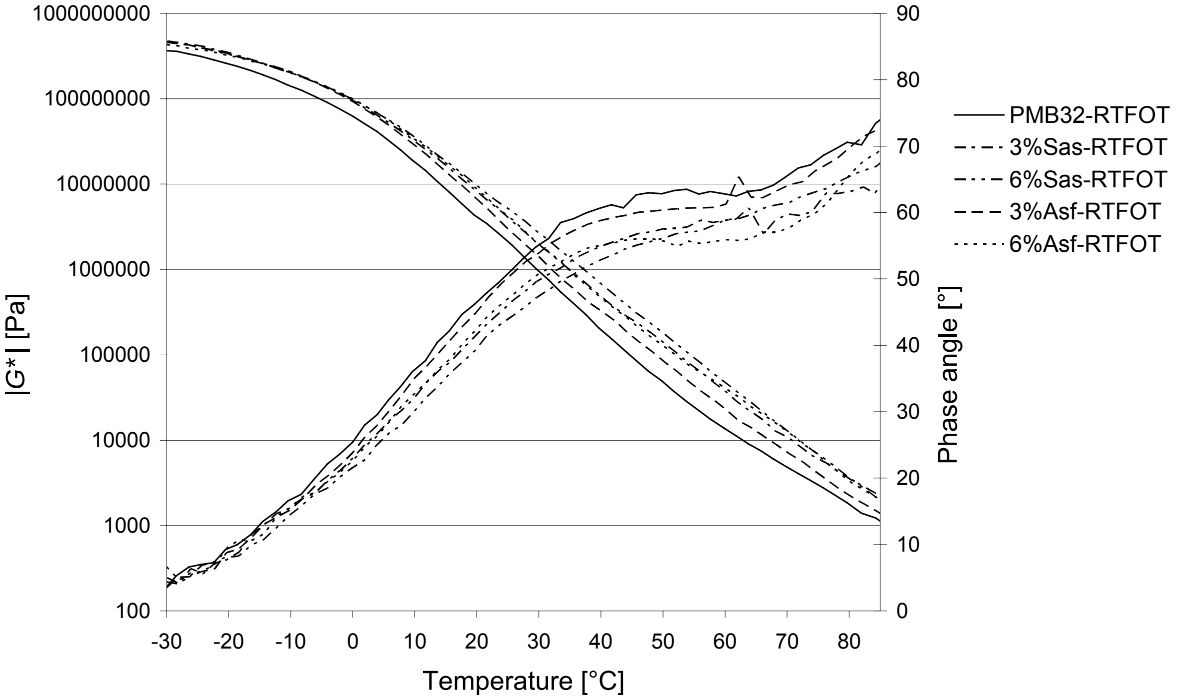

Figure 4 DSR temperature sweep from -30 to 80°C at a frequency of 10 rad/s for Pmb 32 containing wax, after laboratory ageing.

4.3 Conclusions and further work

Based on results for binder mixtures so far in this study, the following preliminary conclusions may be drawn:

- Both waxes (Sasobit and Asphaltan A) have a flow improving/viscosity depressant impact on Pmb 32 at higher temperatures, indicating a possible lower laying temperature for mastic asphalt products if modified with such waxes.
- Concerning binder performance at temperatures lower than approximately 100°C, there is a stiffening effect due to wax modification, indicating a certain positive effect on stability. However, this stiffening effect goes down to at least -18°C. But on the whole, these waxes show little or no negative effect on the low temperature performance of Pmb 32.

Further laboratory testing will be performed on mastic asphalt test specimens containing selected binder mixtures. Indentation value at 40°C will be determined and dimentional stability at 80°C (according to EN 12970, Annex B). The tensile strain restrained specimen test (TSRST) will be performed as well.

5. References

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