

# Lignin as a green alternative for bitumen

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## ABSTRACT

*In 2014, the European bitumen consumption was 11.3 Mt. The paving grade bitumen comprise the greater part of the bitumen consumption (83%). Generally, traditional hot mix asphalt emits large quantities of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O. This material is part of the high carbon emissions disaster area of the high-way industry, which is unfavorable to the development of a low-carbon economy.*

*Another challenge for the bitumen industry is that the petrochemical industry is becoming more and more efficient in breaking down higher chain hydrocarbons to lower chain hydrocarbons with higher added value than bitumen. This has an effect on the availability of bitumen.*

*The asphalt market is looking for alternatives with higher sustainability in terms of CO<sub>2</sub> emission. The usage of alternative sustainable binders, which can (partly) replace the bitumen, contributes to reduce CO<sub>2</sub>-emissions and at the same time broadens the availability of binders.*

*The paper will describe the use of lignin as a “partial” substitute for bitumen. The alternative polymer that has been researched as a “partly” alternative for bitumen originates from nature and is called lignin. Lignin is one of the most abundant natural polymers (next to cellulose and hemicellulose) present in plant material. The chemical structure known today does reflect the structure for bitumen and therefore it could be used as an alternative for bitumen in applications like roofing or asphalt.*

*The paper will describe the proof of concept in using lignin, as replacement or partial replacement of bitumen without losing its functionality. Several types of lignin and bitumen blends have been researched. Not only native lignins but also modified lignins have been researched. These modifications were performed to meet original binder (bitumen) properties or to improve binder properties. For the evaluation of the lignin-bitumen blends properties (chemical and mechanical), techniques such as DSR have been used. In conclusion the paper will describe the results of this evaluation.*

**Keywords:** Environment, Modified Binders, Polymers, Renewable, Rheology

## 1. INTRODUCTION

Bio-based waste is used to improve properties (lifetime of the material) and environmental sustainability by shifting from fossil based resources to bio-based resources. Bio-based resources are in favor from the sustainability point of view: they are renewable and do not contribute to climate change, as CO<sub>2</sub> is captured from the atmosphere as a result of photosynthesis in the original vegetal source.

As bitumen is produced from fossil sources the asphalt market is looking for alternatives with higher sustainability in terms of CO<sub>2</sub> emission. The usage of alternative sustainable binders, which can (partly) replace the bitumen, contributes to reduce CO<sub>2</sub>-emissions.

Another challenge for the bitumen industry is that the petrochemical industry is becoming more and more efficient in breaking down higher chain hydrocarbons to lower chain hydrocarbons with higher added value than bitumen. This has an effect on the availability and quality of bitumen. The use of alternative sustainable binders broadens the availability.

The paper describes the use of lignin as a “partial” substitute for bitumen. The alternative polymer that has been researched as a “partly” alternative for bitumen originates from nature and is called lignin. Lignin is one of the most abundant natural polymers (next to cellulose and hemicellulose) present in plant material. The chemical structure known today does not reflect the structure for bitumen and therefore it could be used as an alternative for bitumen in applications like roofing or asphalt.

The paper describes the proof of concept in using lignin, as replacement or partial replacement of bitumen without losing its functionality. Several types of lignin and bitumen blends have been researched. Not only native lignin's but also modified lignin's have been researched. These modifications were performed to meet original binder (bitumen) properties or to improve binder properties. For the evaluation of the lignin-bitumen blends techniques such as DSR (Dynamic Shear Rheology) have been used. In conclusion the paper describes the results of this evaluation.

## 2. APPROACH

In order to evaluate the use of lignin as a substitute for bitumen various types of lignin have been included. Typical lignin sources such as from wood and straw obtained through the mild extraction process, SHS (SuperHeated Steam), developed by TNO have been used and different types of more robust extraction of the lignin have been used includes Kraft, Organosolv and Klason lignin. These types of lignin and their extraction process will be further described in chapter 3.

The evaluation started with using Organosolv lignin. This type of lignin was blended with different types of bitumen (10/20, 70/100 and 160/220) in various amounts. The blends were evaluated on two main aspects: the miscibility of the lignin in the bitumen and the rheological performance of the blend. What is the influence of the bitumen type and to what extent can lignin be blended without loss of functionality.

The aim of the blending was to come up with a homogenous blend where on a “molecular” level the lignin is blended with the bitumen. This means **no filler** kind of type blending of the lignin. In addition the mechanical performance (rheological behavior) should be equal to the original bitumen, with no loss of quality (defined by rheological performance).

As a next step different types of lignin were included and finally the effect of chemical modified lignin has been evaluated.

## 3. LIGNIN AND ITS DIFFERENT TYPE

The alternative polymer that has been researched as a “partly” alternative for bitumen originates from nature and is called lignin. Lignin is one of the most abundant natural polymers (next to cellulose and hemicellulose) present in plant material. It consists of aromatic rings connected to each other with hydroxylated alkanes. As opposed to carbohydrates lignin is hydrophobic and does not easily degrade. The chemical structure known today does not reflect the structure for bitumen and therefore it could be used as an alternative for bitumen in applications like roofing or asphalt.

One of the most predominant sources of lignin is the paper industry. In the process of paper making tremendous efforts are made to remove as much lignin as possible. The obtained cellulose fibre is known as “wood free” fibre and is

regarded as high quality. Most of our office paper is made from this cellulose fibre. The residue is a side stream called “black liquor” in which lignin is present. The usual process in order to remove lignin from e.g. wood cellulose is called the “Kraft process”. Invented already in 1879 it is still used today. It is based on cooking wood chips under pressure at around 130 °C under alkaline conditions in the presence of sulfide or bisulfide. The result of this process is that both hemi cellulose and lignin are degraded and solubilized in the alkaline solution. During the process the lignin is substituted with sulfur (2 – 3%). The Kraft process is the most widely used process and delivers over 98% of the lignin currently on the market (in total more than 1 million ton of lignin). The sulfur does hamper the use of this type of lignin resulting in limited use of Kraft lignin and it is mainly used for generating energy.

The industry is looking for other extraction methods without the use of sulfur resulting in sulfur free lignin. Up to now several sulfur free processes are known in the scientific literature such as Organosolv (extraction with ethanol), the production of Klason lignin (water insoluble lignin from concentrated acid hydrolysis process), and soda induced extraction of lignin. In all these cases low molecular weight lignin (low melting point) is obtained and volume of these types of lignin is on the increase. At TNO a new process is under design for extracting lignin resulting in lignin without sulfur. This process is based on the use of superheated steam (SHS) combined with a mild extraction of the lignocellulose resulting in sulfur free lignin.

#### 4. INITIAL BLENDING – AN OVERVIEW

To explore the possibility of replacing partially the bitumen by lignin a first set of blending experiments were performed. This first set of blending experiments focused on its possibility to replace bitumen and to which amount, depended on the type of bitumen used.

The blending program consists of three types of bitumen (from hard grade to soft grade) and one type of lignin in two amounts.

The first blending experiments were performed with one type of lignin, Organosolv. The main arguments to start with this type of lignin, were the sulfur free character of the lignin and the melting behavior. In contradiction with other lignin’s, such as Kraft and SHS, it has the property to melt at elevated temperatures (such as 150 °C) and it does not stay in a powder, filler-like type, form (see figures 1 and 2).



**Figure 1 – Example of a powder, filler-like type of lignin**



**Figure 2 – Melted Organosolv lignin after exposure @ 150 °C**

After the first set of experiments Klason, SHS and Kraft lignin were included to extend the evaluation of the effect of the type of lignin used. This was done for one type of bitumen, 70/100 and 25 % (w/w) of lignin in the blend.

An overview of the blending experiments is given in table 1.

**Table 1 – Blending overview**

Type of lignin	Organosolv		Klason	Kraft	SHS
	10 %	25 %	25 %	25 %	25 %
Amount of lignin in the blend (% m/m)					
10/20	X				
70/100	X	X	X	X	X
160/220	X	X			

## 5. BLENDING EXPERIENCE – ORGANOSOLV LIGNIN

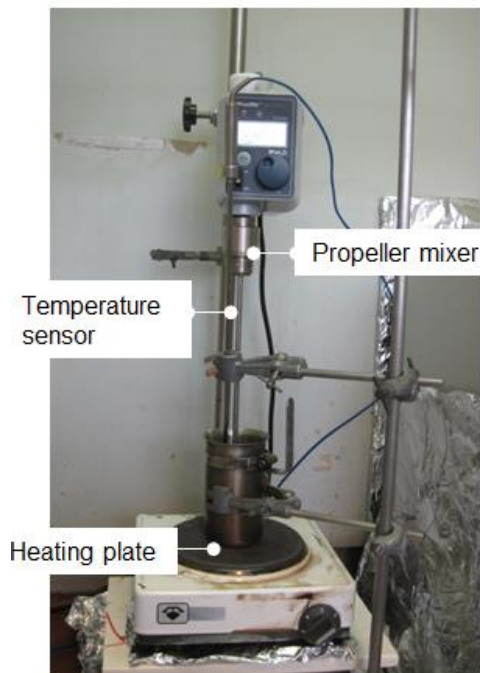
The first blending experiments with Organosolv lignin were performed by blending the lignin by hand, gradually adding the lignin in powder form and increasing the blending temperature during the adding of the lignin to the bitumen. The end blending temperature was different for the different types of bitumen used: 10/20 blends - 185 °C; 70/100 - 155 °C; 160/220 - 145 °C.

**Table 2 – Organosolv lignin blending experience**

Blend	Miscibility	Coagulation
10/20 10 % (w/w) Organosolv	+	-
70/100 10 % (w/w) Organosolv	+	-
160/220 10 % (w/w) Organosolv	+	-
70/100 25 % (w/w) Organosolv	0	+
160/220 25 % (w/w) Organosolv	0	+
+	Good	Occurs
0	Average	Occurs (less)
-	Bad	Does not occur

It was noticed that adding 10% of Organosolv lignin to the bitumen gave no problems on miscibility and coagulation. Increasing the amount of lignin up to 25% (w/w) in the blend gave a minor form of coagulation of the lignin. Blending 10 to 25% (w/w) lignin with bitumen was found to be possible, at 25% (w/w) mixing by hand it seems to become critical for the Organosolv lignin.

Based on the first blending procedure experience the procedure for blending was modified. To avoid coagulation of the lignin, the adding of the lignin was done by using a sieve. A finer distribution and contact with the bitumen is hereby achieved. The lignin should be equally fine distributed on the bitumen surface. Also the blending by hand was replaced by low shear blending using a propeller mixer (see figure 3). And finally a constant blending temperature, tuned on the different bitumen types, was applied resulting in homogeneous blends.



**Figure 3 – Set-up for blending the lignin with bitumen**

To evaluate the modification of the blending procedure, the Organosolv 25 % (w/w) blending was repeated using this procedure. The characterization of the blend (low-shear) by using DSR (Dynamic Shear Rheology) gave comparable results with the hand blended blend. Based on those results it was concluded that the new blending procedure could be used for further research. The Kraft, Klason and SHS lignin blends were prepared using the low shear procedure.

## **6. CHARACTERIZING BLENDS USING DYNAMIC SHEAR RHEOMETER (DSR)**

To characterize the blends DSR measurements, strain sweeps followed by frequency sweeps were performed in the range of -10 to 60°C, at a frequency of 0,1 to 400 rad/s. The data was used for making master curves of the complex modulus ( $G^*$ ) and the phase angle ( $\delta$ ) at a reference temperature of 20°C, using the Time Temperature Superposition-principle. The resulting master curves were used to evaluate the effect of the amount of lignin in relation to the used types of bitumen.

### **6.1 Evaluation of the 10% Organosolv blends on the different bitumen types**

In figures 4 and 5 an overlay is given for the used reference bitumen, 10/20, 70/100 and 160/220 and the corresponding bitumen blends with 10% of Organosolv lignin.

As can be seen from figures 4 and 5, for the harder type of bitumen 10/20 an effect of increasing stiffness and decreasing phase angle at lower reduced frequencies is observed. This effect is not seen for the softer bitumen types 70/100 and 160/220. Based on the master curves it can be concluded that adding 10% by mass of lignin has no effect on the rheological behavior of the base bitumen using softer kinds of bitumen. For harder bitumen types the addition of lignin results in increasing the stiffness and reducing the phase angles especially at lower frequencies.

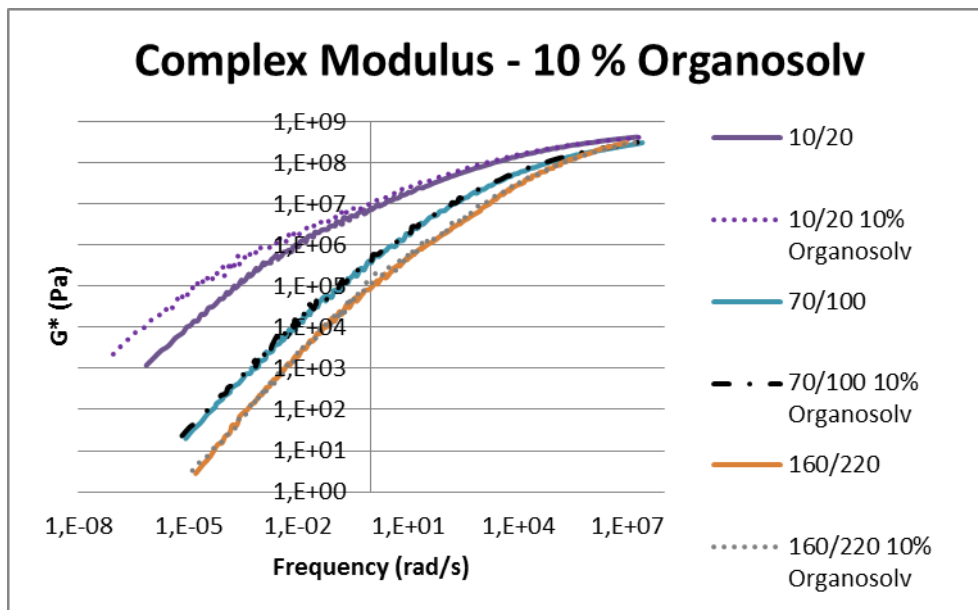


Figure 4 – Complex Modulus – Overlay reference and 10% Organosolv lignin blends

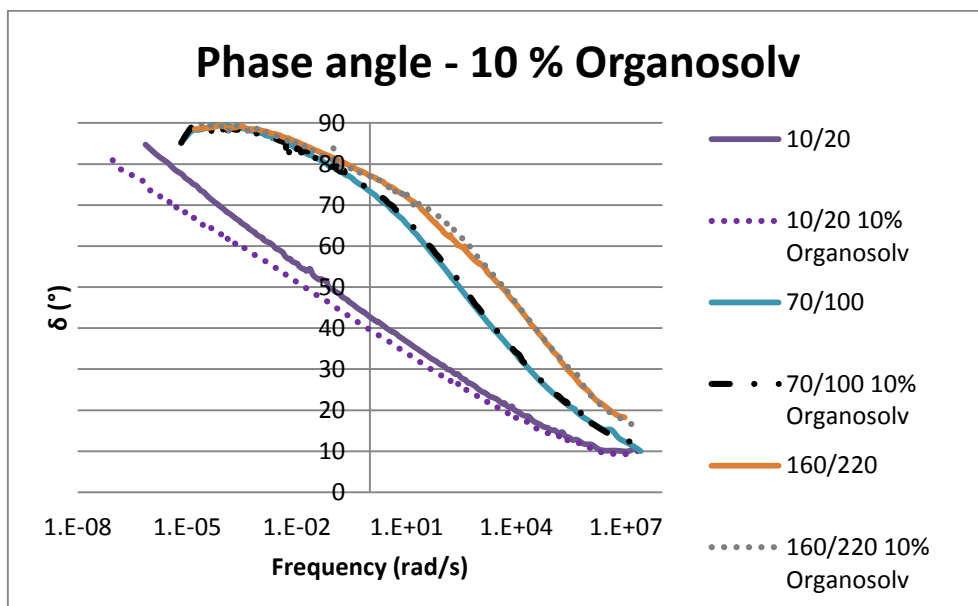


Figure 5 – Phase angle - Overlay reference and 10% Organosolv lignin blends

## 6.2 Evaluation of the amount of Organosolv blended with different types of bitumen

As seen in figures 4 and 5, adding 10 % (w/w) of lignin to the softer binders has no effect on the visco-elastic behavior. Increasing the amount of Organosolv lignin up the 25% for the bitumen 70/100 and 160/220 has a significant effect. As an example this can be seen in figures 6 and 7. With 10 % of lignin there is no effect, but with 25% of lignin there is a clear increase of stiffness. The increase of stiffness by adding lignin is also found in other literature [1,2]. Also the phase angle changes if 25% of lignin is present in the blend. A polymer type like behavior of the blend can be observed. Similar observation were done for the 160/220 with 25% of lignin blend.

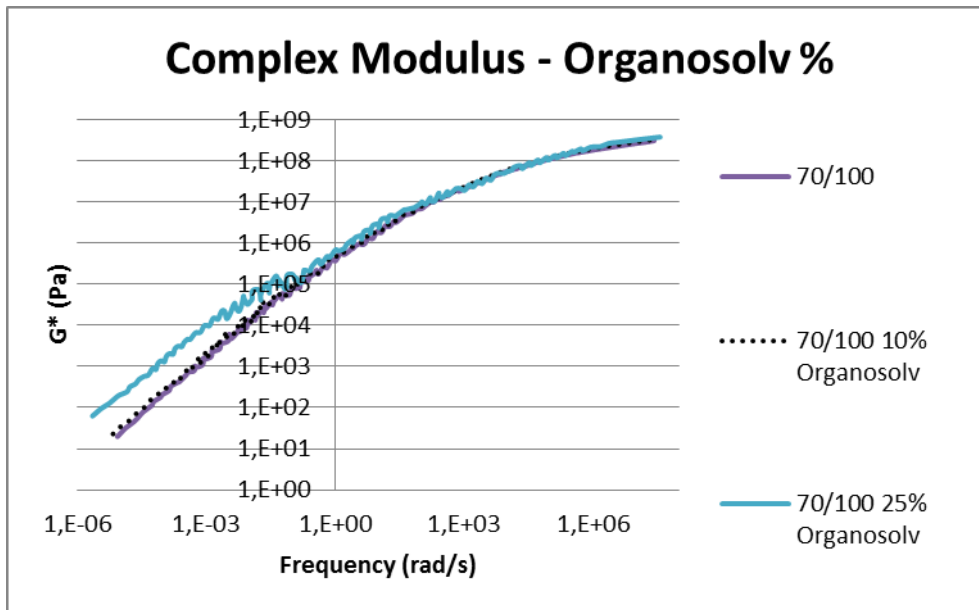


Figure 6 – Complex Modulus – Overlay reference and Organosolv lignin blends, effect of amount of lignin in the blend

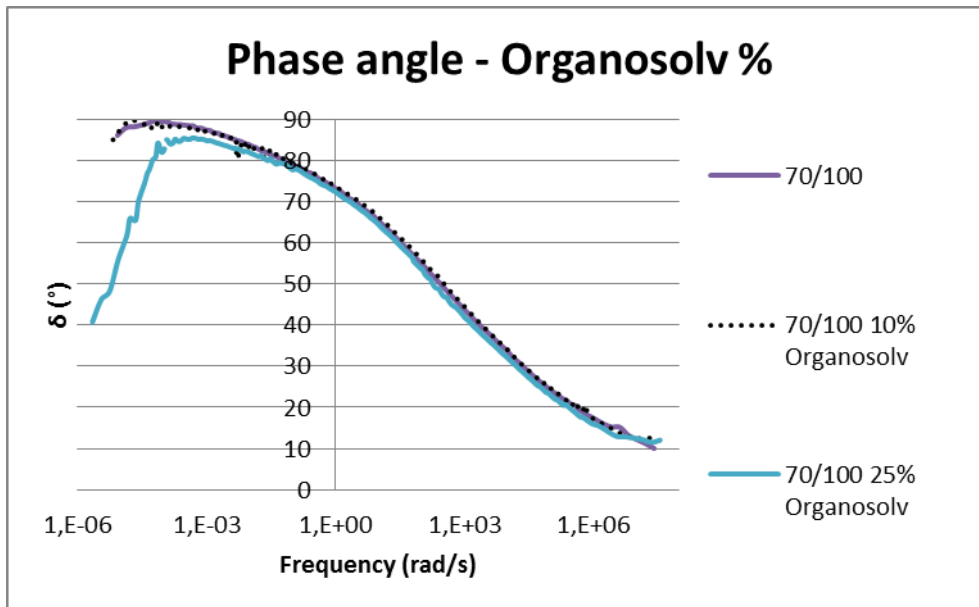


Figure 7 – Phase angle – Overlay reference and Organosolv lignin blends, effect of amount of lignin in the blend

It can be concluded that increasing the amount of lignin has a significant effect on the rheological behavior of the blend, compared to the original bitumen. For harder types of bitumen this is already seen at lower lignin concentrations (10%) in the blend. For softer types of bitumen this effect is noticeable at higher lignin concentrations (25%). Adding small amounts of lignin (10%) to soft binders does not seem to effect the rheological behavior.

### 6.3 Evaluation of the type of lignin used in the blend

After the first set of experiments with Organosolv lignin's Klason, SHS and Kraft lignin were included to expand the evaluation of the effect of the type of lignin used. This was done for one type of bitumen, 70/100 and 25 % (w/w %) of lignin in the blend. The blends were made using the low shear blending as described in chapter 5.

After preparing, the blends were characterized with DSR. The result of the different blends can be seen in figures 8 and 9.

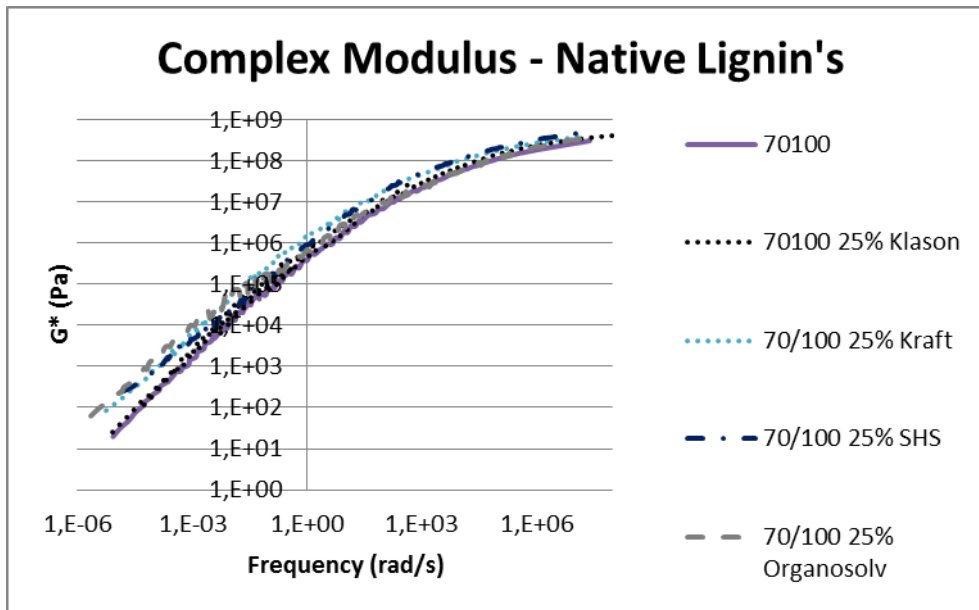


Figure 8 – Complex Modulus – Overlay reference and 70/100 25% lignin blends, effect of lignin type

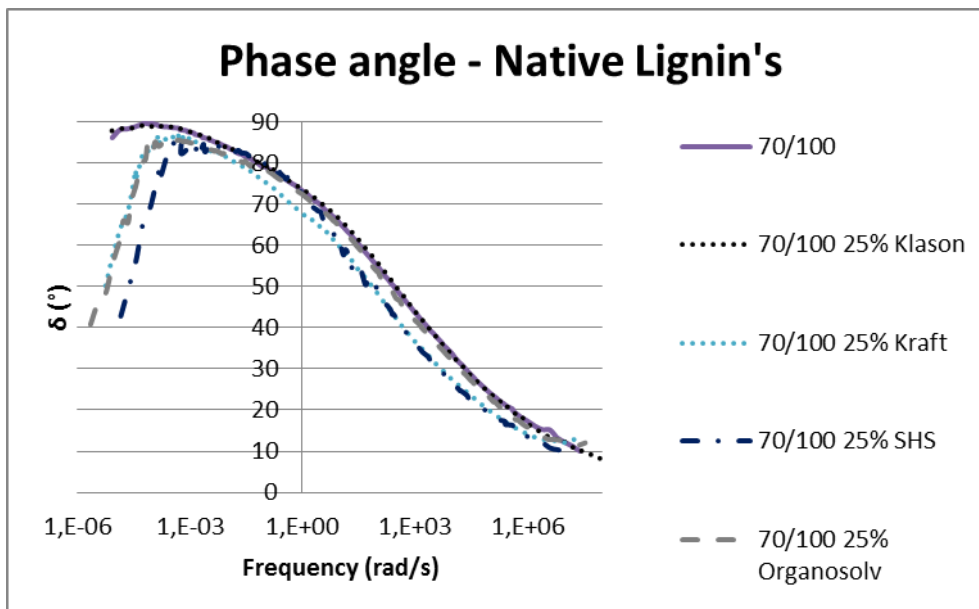


Figure 9 – Phase angle – Overlay reference and 70/100 25% lignin blends, effect of lignin type

Several types of lignin Organosolv, Klason, SHS and Kraft have been explored on a larger scale. All these lignin's were found to be suitable for blending with bitumen. In general analysis shows an increase of stiffness compared to the reference binder, except for the Klason lignin. This type of lignin has a comparable visco-elastic behavior as the reference bitumen. Just as the Organosolv also the SHS and Kraft shows a change in phase angle. It has the tendency to behave like polymer modified bitumen such as SBS. The Klason lignin is comparable with the 70/100 reference bitumen. Based on these observations it can be concluded that the type of lignin (extraction method) has an influence on the visco-elastic behavior. For replacing 25% (w/w) of the used 70/100 bitumen with lignin with equal visco-elastic behavior, the Klason lignin is preferred. Using the other types, Organosolv, SHS or Kraft, a behavior is found comparable with Polymer Modified Bitumen (PMB). These types could be potential alternatives for an application where normally PMB's are used, for instance in road application with improved rutting resistance or for roofing applications.



## 7. MODIFICATION OF THE LIGNIN

Compared to bitumen lignin has a high amount of hydroxyl groups. To make lignin even more hydrophobic and more compatible with bitumen the hydroxyl groups present in the lignin (see figure 10) have been blocked by using hydrophobic substituents. Several modification routes have been explored using commercially available epoxide containing reactants under alkaline conditions. An epoxide with a more aromatic character, FGE (Phenylglycidyl ether), has been used; and an epoxide with a more aliphatic character, EGE (Ethylhexylglycidyl ether), has been used. The lignin used for the chemical modification was the Organosolv lignin.

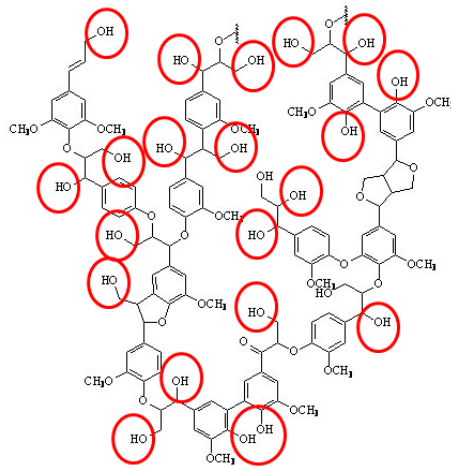
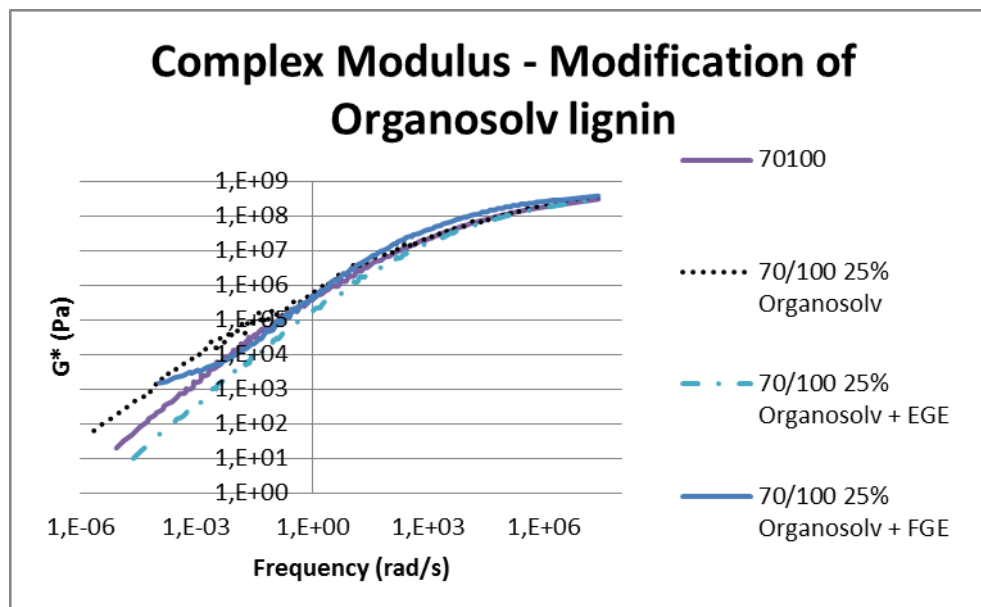


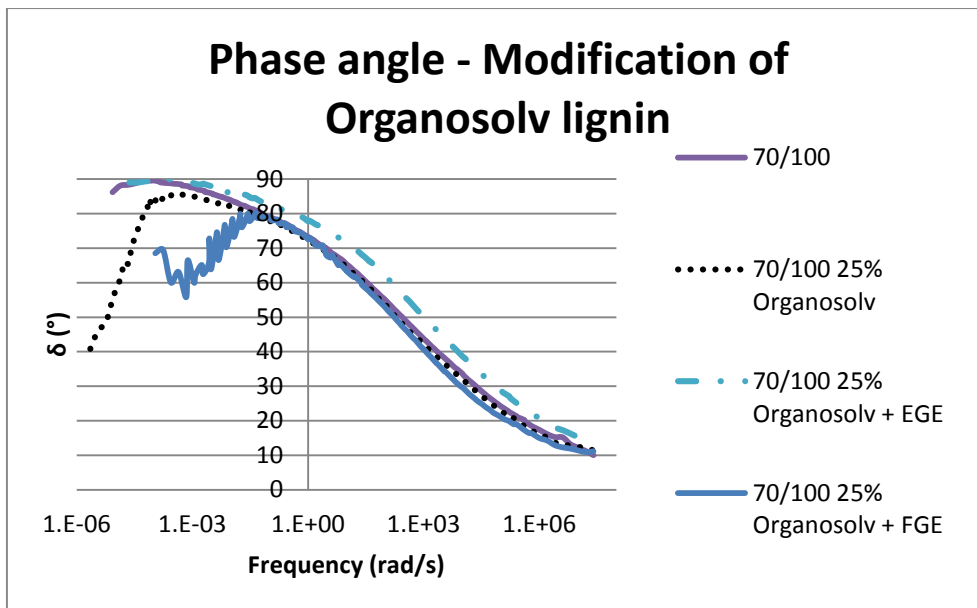
Figure 10 – Hydroxyl groups present in lignin

The modified lignin's were blended with the 70/100 bitumen resulting in 25% (w/w) of modified lignin. The result of these modifications is that indeed the modified lignin's were easily blended. The modification might even help to increase the amount of lignin that can be blended with the bitumen.

After preparing, the blends were characterized with DSR. The result of the different blends can be seen in figures 11 and 12.



Figures 11 – Complex Modulus – Overlay reference and 70/100 25% lignin blends, effect of modification of Organosolv lignin



**Figure 12 – Phase angle – Overlay reference and 70/100 25% lignin blends, effect of modification of Organosolv lignin**

In figure 11 the effect of the native Organosolv lignin is visible. As seen as before the stiffness increases compared to the reference bitumen. Modifying the lignin with EGE, results in decreasing the stiffness and increasing the phase angle. The polymer effect of the native organosolv lignin has been eliminated by modifying the lignin with EGE. This in contradiction with the FGE modified Organosolv lignin, here clearly can be seen that the polymer effect has increased due to the more aromatic epoxide modification. Based on this modification route it can be concluded that the visco-elastic behavior of the bitumen lignin blend can be directed by using different types of epoxide.

## 8. OVERALL CONCLUSIONS

Lignin which originates from Organosolv, Klason, SHS and Kraft are miscible with the used bitumen fraction up to 25% .

DSR analysis show that the type and amount of lignin effects the visco-elastic behavior.

The effects differs for the different types of lignin. Most of the used native lignin types (Organosolv, Kraft and SHS) blended with a significant amount (25% w/w) show polymer like behavior and therefore adding functionally to the binder.

With increasing concentration of the lignin amount in the blend the effects become bigger; significant changes in stiffness and phase angle have been observed.

The effect does not only depend on the amount of lignin, but also on the type of bitumen used. Smaller amounts do sooner have an effect when blended with harder bitumen grades.

By modifying lignin it's possible to adjust the visco-elastic behavior of the lignin-bitumen blend, where EGE modification leads to conventional bitumen visco-elastic behavior and FGE modification leads to more PMB visco-elastic behavior.

## ACKNOWLEDGEMENTS

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