TALLINN UNIVERSITY OF TECHNOLOGY

MAANTEEAMET

Bitumen research in Estonia

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Consultants

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- Queens University – Prof. Simon Hesp;
- Delft University;
- Norwegian University of Science and Technology (NTNU);

Motivation

- Feedback from the field:
  - Contractors have told that bitumen 70/100 for AC is not the same than some years ago;
  - EN test results are always in the required limits and shows no significant differences.
    - In the reality differences can be significant;
  - For surface dressing – bitumen is very brittle around „0“ degrees and especially first winter is problematic;
  - Work quality differs in the same conditions within two years in row;
- We see some defects (cracks) already after 2…4 years but according to EN everything is OK;

- Is it about the binder?
  - the most expensive component in AC;
  - component with the least knowledge.
- Are EN tests for bitumen properties and quality control enough or do we need something else?
  - Different approach?
- What is GOOD binder?
  - The properties, limits, measurements?

- Improvement of bitumen knowledge in Estonia;
  - Overall knowledge has been poor even in the sense of basic EN tests.
- We would like to have more information about what we are dealing with.
  - Bitumen is not an black mysterious liquid;
  - Bitumen is an important product for long lasting roads.

Hypothesis

- Bitumen quality in Estonia is poor or have gotten worse over the years;
- Tests done in our labs (according to EN) does not represent bitumen real behavior and we are unable to predict pavement performance;
- Performance grade (PG) tests gives the information what we need;

Description

- 8 binders present in Estonian market:
  - 5 binders 70/100;
  - 2 binders 160/220;
  - 1 Estonian oil shale binder.

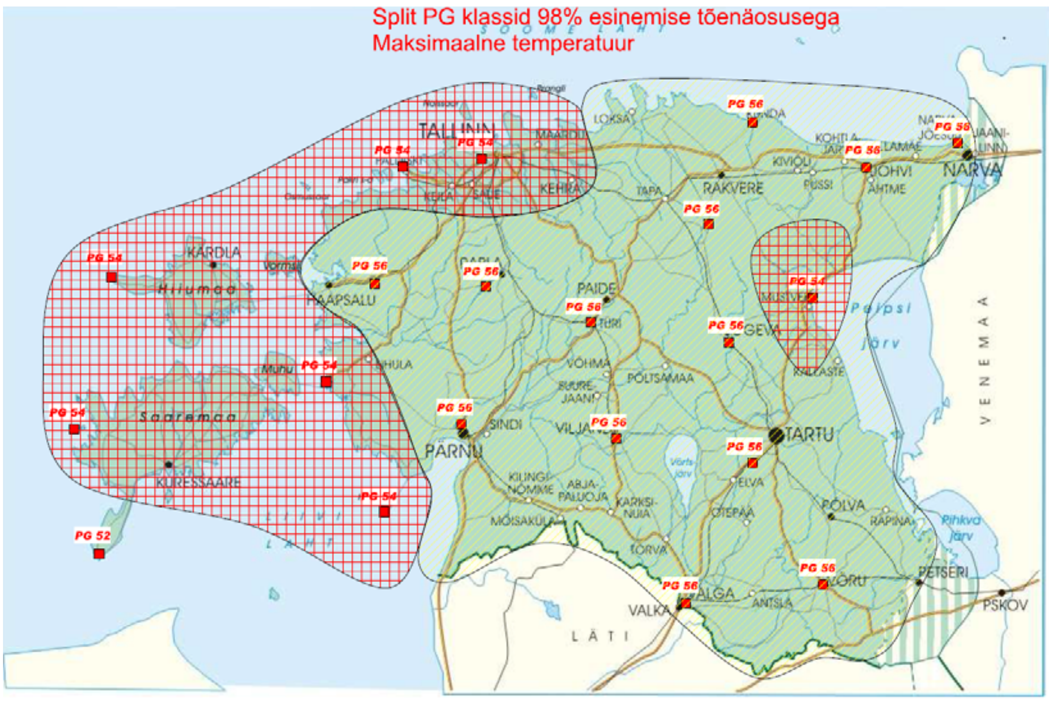
- To evaluate these properties:
  - All tests by EN-normative;
  - North-American PG + needed modification to meet the requirements;
  - Extra testing proposed for PG modification – LAS, SENB, MSCR;
  - PG and physical hardening (eBBR, mPAV, DENT) + needed modification to meet the requirements;
  - Chemistry (elemental composition, FTIR, GC-MS, GPC, NMR, DSC, TGA, SARA).

EN results

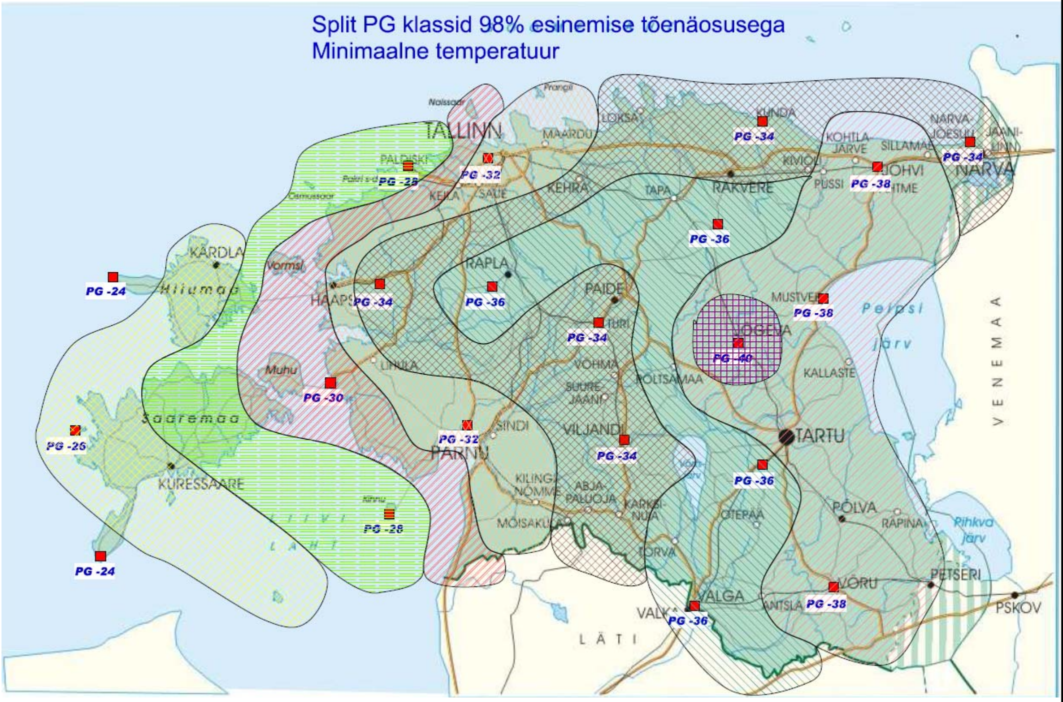
nr	Measured properties	Unit	70/100					160/220		Oil shale
			A	B	C	D	E	F	G	H
1	Penetration	x 0,1 mm	84	74	83	88	82	177	186	319
2	Softening point (R&B)	˚C	45,4	46,6	45,8	46,4	52	38,2	38,8	30,8
3	Kin. visc 135 ˚C	mm^2/s	368	382	357	358	660	212	191	43
4	Dyn. visc 60 ˚C	Pa x s	180	161	139	134	358	63	43	11
5	RTFOT mass loss	%	-0,17	0	0,11	0,05	0,01	-0,42	0,16	-2,4
6	Penetration after RTFOT	x 0,1 mm	54	50	54	61	56	108	119	88
7	Softening point after RTFOT	˚C	51,2	51,6	50,6	51,2	59,6	44,2	43,6	41,4
8	Retained penetration after RTFOT	%	64	68	65	69	68	61	64	28
9	Change in softering point after RTFOT	˚C	5,8	5,0	4,8	4,8	7,6	6,0	4,8	10,6
10	Elastic recovery @ 10 ˚C	%	20	12	14	13	18	16	11	1
11	Breaking point (fraas)	˚C	-16	-15	-20	-18	-24	-20	-18	-12
12	Flashpoint	˚C	316	276	352	338	316	294	344	254
13	Solubility in toluene	%	99,98	100	99,98	99,97	99,98	99,99	99,98	99,98
14	Penetration index	-	-1,2	-1,2	-1,1	-0,7	0,6	-1,4	-0,9	-3,3
15.1	Ductility @ 5 ºC	J/cm^2	5,17	-	6,07	4,33	-	1,40	2,6	-
15.2	Ductility @ 10 ºC		-	2,35	-	-	1,60	-	-	-
15.3	Ductility @ 15 ºC		-	-	-	-	1,00	-	-	0,52

- Binder E has a high PI and fails the ductility test at 5°C which indicates it is elastic due to the air blowing and this is known to give early and excessive cracking distress in service.
- Ductility is likely a very good performance-based indicator if done at low temperatures (5-15°C). The pavements containing asphalt with low ductilities are likely to show poorer service than pavements containing asphalts of the same penetration but with high ductilities. (Kandhal 1977)

PG HT split
+52
+54
+56



PG LT split
-24
-28
-30
-32
-34
-36
-38
-40



Binder	Split PG	
	HT	LT
A	64	-24
B	62	-24
C	60	-24
D	62	-28
E	68	-32
F	56	-30
G	52	-28
H	52	-12

Modification – UW-MARC

A – bio oil;
B – VTEA/REOB

Base binder	Modification	Modified binder
A	5% A	M-A
B	10% B + 2% plastomer	M-B
C	8% B + 3% SBS	M-C
D	8% B + 2% plastomer	M-D
E	11% A	M-E-1
E	8% B	M-E-2
F	8% B + 4% plastomer	M-F
G	8% B + 5% SBS	M-G

Binder	Split PG	
	HT	LT
M-A	58	-28
M-B	58	-38
M-C	60	-36
M-D	62	-38
M-E-1	60	-36
M-E-2	58	-42
M-F	62	-36
M-G	58	-38

Bituumen	Penetration		Softening point (°C)		Breaking point (°C)	
	Neat	Modified	Neat	Modified	Neat	Modified
A	84	187	45,4	37,8	-16	-24
B	74	203	46,6	53,0	-15	-29
C	83	217	45,8	40,4	-20	-26
D	88	150	46,4	51,6	-18	-29
E-1	82	168	52,0	44,6	-24	-31
E-2	82	187	52,0	43,4	-24	-31
F	177	240	38,2	49,6	-20	-27
G	186	225	38,8	33,4	-18	-27

Oil and hybrid modification?

- Using waste and vegetable oils are threath for **premature hardening** through gel formation, volatilization, exudation (sweating of oils) and oxidation.
  - The typically large amounts of paraffin in waste oil residue make the asphaltene fraction less soluble in the maltene phase and this in turn predisposes the binder to accelerated physical and chemical hardening. (Hesp & Shurvell 2012)
  - TOP (by-product of the pulp and paper industry) caused an increase in the ageing index and a reduction in the resistance to oxidative hardening (*similar effects is anticipated in vegetable oil modified asphalt since both have multiple double bonds and are flocculants to asphaltenes*). (Shean et.al 2007)
  - Problems have occurred with binders containing both SBS and REOB (it contains polyisobutylene which precipitates the SBS which can lead to serious failures). (Wright et.al 2011)

- Reversible hardening can broadly be defined as the gradual stiffening of a material during isothermal storage at low temperatures brought about by changes in bitumen structure (wax crystallization, asphaltene aggregation, volume relaxation) (Hesp et.al 2007)

- The effects of physical and chemical hardening are very similar. Both processes originate from the imbalance between the solubility properties of the asphaltenes and the maltenes.
- When maltenes lack the aromaticity to solvate or peptize asphaltenes, a gel type structure is formed with a high viscosity at low temperatures, leading to premature and excessive thermal cracking. (Erskine et.al 2012).

Different view on using oil modification

- The amount of recycled engine oil Hesp used in his study — between 15 and 30 percent of the asphalt – far exceeds what is commonly in asphalt, that is less than 8 percent. (Commonwealth magazine „Laying it down, testing it later“. Fall 2014)

- “Our study indicated that there isn’t any rapid hardening in the asphalt binder or mix with VTAE and when we evaluated the chemistry, the data clearly shows that there are no cancer causing materials in the VTAE“ (Asphalttopics, ohmpa „The Straight Goods on Vacuum Tower Asphalt Extenders in Asphalt Cement“. Fall 2014)

- Considering that
  - „Reversible aging at low temperatures is a likely and serious cause of premature and excessive cracking at low temperatures. A 6 °C loss in low-temperature grade due to this process will reduce the confidence that a given road will not be exposed to damaging temperatures from the intended 98% to less than 50%." (Hesp et.al 2007);
- We wanted to have a closer look on that.

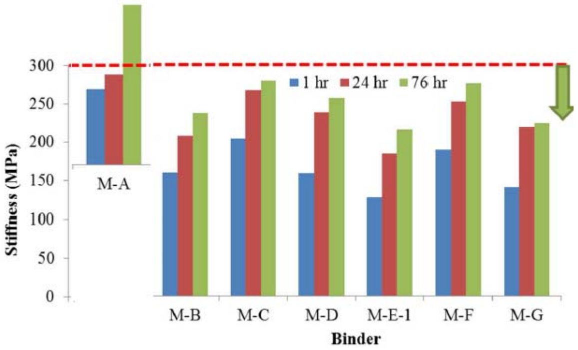
Reversible hardening

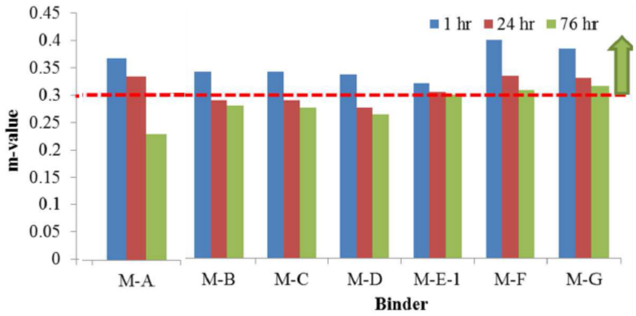
- **LS-308 (eBBR)** conditions at 10°C and 20°C above the minimum design pavement temperature for periods of 1 h, 24 h, and 72 h to simulate the effect of extended exposure to two different cold temperatures.
  - Investigation of 20 paving contracts in eastern and northeastern Ontario, Canada, found that by measuring the creep properties after 1, 24, and 72 h of conditioning, according to LS-308, the accuracy of the performance grading increased from 55% (BBR) to a range of 90% to 95% (eBBR), depending on the exact specification criteria that were chosen (Hesp, Soleimani et.al 2009)

LAB CODE	SUPERPAVE LIMITING TEMPERATURES, °C					SUPERPAVE GRADE	SUPERPAVE GRADE SPAN	DSR ON PAV RESIDUES			LS-308 EBBR RESULTS, °C	
	DSR_0	DSR_{RTFO}	DSR_{PAV}	$BBR_{S(60s)}$	$BBR_{m(60s)}$	XX-II-YY		DSR_{PAV20} $G^*/\sin\delta$ = 2.2 kPa	DSR_{PAV40} $G^*\sin\delta$ = 5.0 MPa	DSR_{PAV40} $G^*/\sin\delta$ = 2.2 kPa	72 h Grade	72 h Loss
A	64,4	63,0	17,7	-17,2	-20,6	63-18-27	90	71	23	77	-26,9	0,3
B	64,4	62,7	17,7	-17,9	-17,9	63-18-28	91	70	22	77	-21,3	6,6
C	64,1	63,5	18,5	-18,6	-18,1	64-19-28	92	71	21	78	-23,1	5,0
D	61,6	61,6	18,2	-20,3	-19,8	62-18-30	91	69	20	77	-22,9	6,9
E	68,6	70,0	13,3	-24,9	-21,3	69-13-31	100	81	16	93	-24,2	7,1
F	56,3	55,9	12,6	-21,6	-23,5	56-13-32	88	63	13	69	-31,3	0,3
G	53,9	52,9	14,6	-18,5	-20,7	53-15-29	82	58	16	63	-23,3	5,1

- Samples were conditioned at their LT+10°C for 24 and 72 hours;
- Binders tested in 3 categories based on LT grade.

- BBR at **-18°C (binder M-A)** and -24°C (M-B…M-G):





m-value is the controlling factor

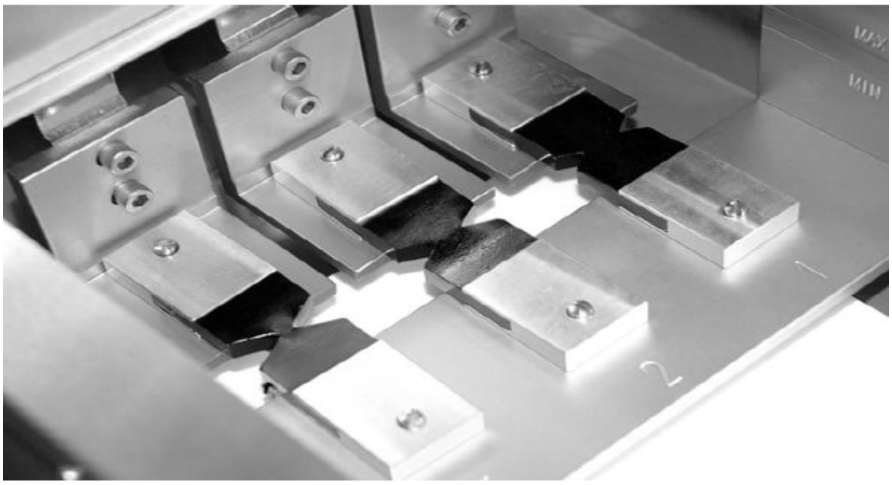
- **Higher polymer content showed to be more effective**
  - compare C ja G which are from the same crude and which has very similar physichal hardening figures for unmodified state;

- *Lack for significant thermal cracking distress was likely due to high polymer content providing a significant strain tolerance. (Wright et.al 2011)*
- *Santagata et al. (1996) studied 16 different modified binders and concluded that no simple effect of the polymer modifier can be found and that different polymers have "widely different effects on the aging rates". EVA copolymers were found to make the hardening worse, while EMA and SBS copolymers were found to lessen it.*
- *Polymers such as SBS can increase the elasticity of the neat binder which results in higher endurance and reduce the susceptibility to thermal and fatigue cracking (Brule, 1997), (Yildrim, 2007)*

- **Adding oil made physical hardening worse**
  - compare A ja F which are from the same crude and which has very similar physichal hardening figures for unmodified state;
- *WEO should only be used with great caution for the modification of low asphaltene binders (Johnson and Hesp)*

Reversible hardening and fatigue

- **LS-299 (DENT,** Double Edge Notched Tension**)** allowes to determine the fracture properties of asphalt cement at brittle-to-ductile and ductile states.
- Both the essential and plastic works of fracture as well as the critical crack opening displacement (CTOD) need to be high in order to provide a high resistance to fatigue and other types of fracture distress. (Hesp et.al 2009).
- The data indicate a general tendency for asphalt cements with high CTODs to show little or no cracking in service. In contrast, a majority of the severely cracked contracts show CTODs that are low. (Ahmed et. al 2012)
- It is shown that high correlations exist between the CTOD and the fatigue properties of the asphalt cement and has an accuracy of 85 percent to predict fatigue cracking and ductile fracture properties of both binders and mixtures (Subramani 2009)



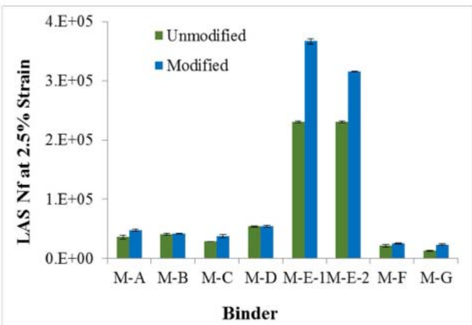
Picture: Soleimani, A.; *Use of Dynamic Phase Angle and Complex Modulus for the Low Temperature Performance Grading of Asphalt Cements*, MSc. Thesis, Department of Chemistry, Queen’s University, Kingston, Canada, 2009.

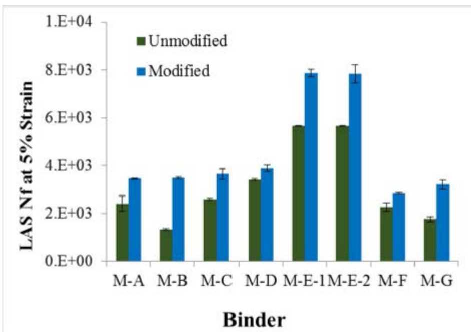
LAB CODE	LS-299 DENT RESULTS												LS-228 MODIFIED PAV (40 HR), °C	
	5°C			10°C			15°C			20°C			$BBR_{S(60\ s)}$	$BBR_{m(60\ s)}$
	w_e, kJ.m^{-2}	βw_p, MJ.m^{-3}	CTOD, mm	w_e, kJ.m^{-2}	βw_p, MJ.m^{-3}	CTOD, mm	w_e, kJ.m^{-2}	βw_p, MJ.m^{-3}	CTOD, mm	w_e, kJ.m^{-2}	βw_p, MJ.m^{-3}	CTOD, mm		
A	BRITTLE FAILURE			24,9	0,53	14,3	15,8	0,34	16,7				-16,6	-18,5
B				BRITTLE FAILURE			15,7	0,47	11,9	7,1	0,06	19,3	-17,4	-15,9
C				BRITTLE FAILURE			15,5	0,43	13,3	9,4	0,18	16,6	-17,3	-16,3
D	BRITTLE FAILURE			15,6	0,70	9,3	10,8	0,31	12,7				-19,6	-17,7
E	BRITTLE FAILURE			16	0,21	10,1	8,2	0,29	10,1				-23,8	-18,2
F	23,6	0,48	15,3	14,2	0,14	19,8	6,3	0,02	26,3				-21,1	-23,8
G	BRITTLE FAILURE			17,3	0,45	13,4	8,3	0,04	23,1				-18,4	-20,1

Materials that fail in LS-308 (eBBR) can still do well in LS-299 (DENT). Hence, LS-299 should be used primarily to screen out asphalt cements that pass LS-308 but that are likely to fail through ductile mechanisms.

Fatigue properties LAS vs DENT

- Linear Amplitude Sweep test is used to evaluate the ability of an asphalt binder to resist fatigue damage by applying cyclic loading at increased amplitudes in order to accelerate damage;
- LAS test has been proposed as an alternative for PG IT test





Binder E does well in LAS but likely would perform very poorly in service due to a lack of durability.

mPAV

- The PAV was meant to produce materials for low temperature and fatigue performance grading with properties similar to those reached after 8-10 years of service. Despite a vast amount of literature that discusses the chemical aging of bitumens, the currently used PAV protocol still fails to replicate the aging process as it occurs in service. (Erskine et.al 2012)

- mPAV refers to accelerated aging according to AASHTO R 28 (PAV) with no testing modifications (Method A); using a reduced film thickness of approximately 0.8 mm in the presence of moisture (Method B); and increasing the aging time to 40 hours with the standard film thickness in the presence of moisture (Method C). (LS 228).

LAB CODE	VE LIMITING TEMPERA		LS-228 MODIFIED PAV (40 HR), °C	
	$BBR_{S(60s)}$	$BBR_{m(60s)}$	$BBR_{S(60\ s)}$	$BBR_{m(60\ s)}$
A	-17,2	-20,6	-16,6	-18,5
B	-17,9	-17,9	-17,4	-15,9
C	-18,6	-18,1	-17,3	-16,3
D	-20,3	-19,8	-19,6	-17,7
E	-24,9	-21,3	-23,8	-18,2
F	-21,6	-23,5	-21,1	-23,8
G	-18,5	-20,7	-18,4	-20,1

Chemical study

- Bitumen is very complex material and describing it in the sense of chemical composition is not an easy task;

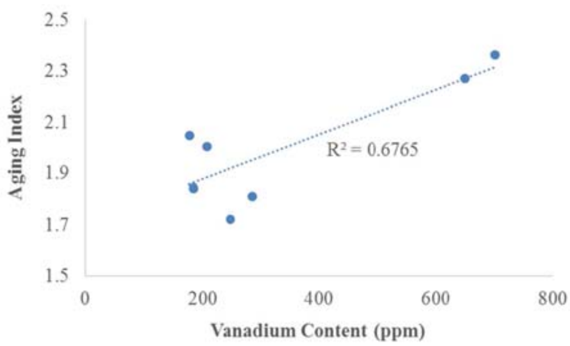
- Many efforts has been done in the sense of explaining bitumen behavior with chemical composition. Not always it has been successful;

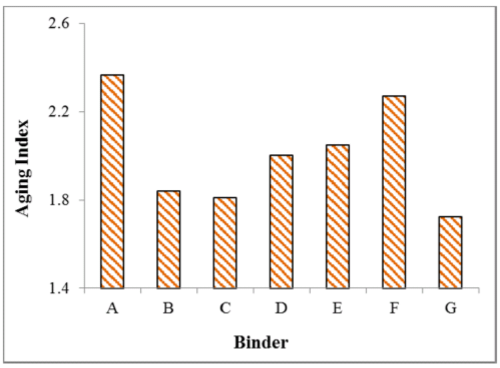
- Our aim was to conduct the tests what are available in Estonia and that set the limit;
- Generally rheology is safer and easier way to describe bitumen but as for this study we were looking for reasons why one or another bitumen behaved like it did and can we link something with each other.

- Elemental composition -> bitumen fingerprint and oxidation;
  - Additional X-ray study showed no Zn and Mo content -> no REOB in our bitumen.

Bitumen	A	B	C	D	E	F	G	H
C (%)	85.17	85.54	85.29	85.29	85.34	85.07	85.23	84.02
H (%)	10.33	10.51	10.46	10.50	10.49	10.39	10.61	8.99
N (%)	0.56	0.56	0.53	0.52	0.47	0.51	0.53	0.16
S (%)	2.99	2.56	2.95	2.82	2.68	2.99	2.84	0.47
O* (%)	0.95	0.84	0.77	0.88	1.01	1.04	0.79	6.35
H/C (atomic)	1.46	1.47	1.47	1.48	1.48	1.47	1.49	1.28
V, ppm	701.9	184.9	285.1	207.3	177.8	649.9	248.0	0.2
Ni, ppm	74.0	48.8	51.9	47.5	36.5	60.5	49.3	1.9
Fe, ppm	17.6	27.8	63.4	33.4	45.7	15.0	78.6	15.5
Na, ppm	22.2	31.4	22.8	13.7	12.9	18.7	20.8	2.2
Mg, ppm	15.2	1.8	1.5	4.7	1.5	24.9	0.9	2.5
Ca, ppm	7.9	5.3	3.4	7.8	4.0	6.8	4.1	22.6
Cu, ppm	0.39	0.59	0.97	0.59	0.67	0.31	0.33	0.39
Pb, ppm	0.09	0.07	0.13	0.16	0.39	0.10	0.10	0.22
Cd, ppm	0.02	0.02	0.03	0.02	0.02	0.01	0.01	0.02

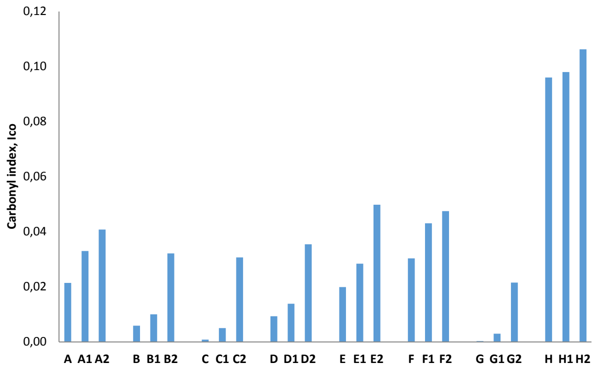
Vanadium is known to promote the ageing of bitumen through oxidation of the carbon matrix (Lesueur 2009);

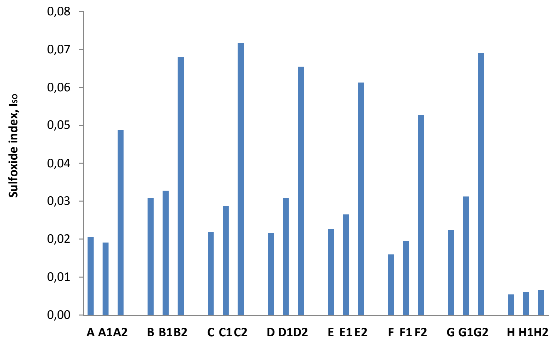




$$Aging\ Index = \frac{RTFO\ Aged\ |G*|/sin\delta}{Un-aged\ |G*|/sin\delta}$$

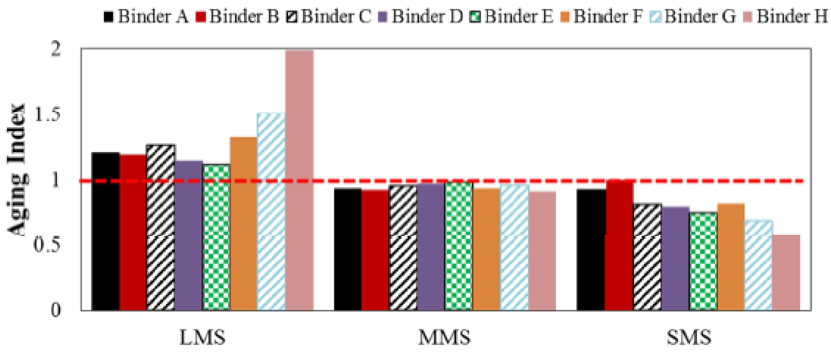
- FTIR spectroscopy -> fingerprint, what is happening during ageing and indication is bitumen straight run or air-blown.
    - Asphalts with insufficient aromatic maltene fractions, asphaltenes are not well dispersed and can agglomerate into connected structures, which form a continuous network throughout the asphalt in extreme cases. These kinds of asphalts are called *gel-type asphalts*. They have low temperature susceptibilities, low ductility, significant thixotropic properties and elasticities, and high rates of age hardening (Hesp et.al 2007)



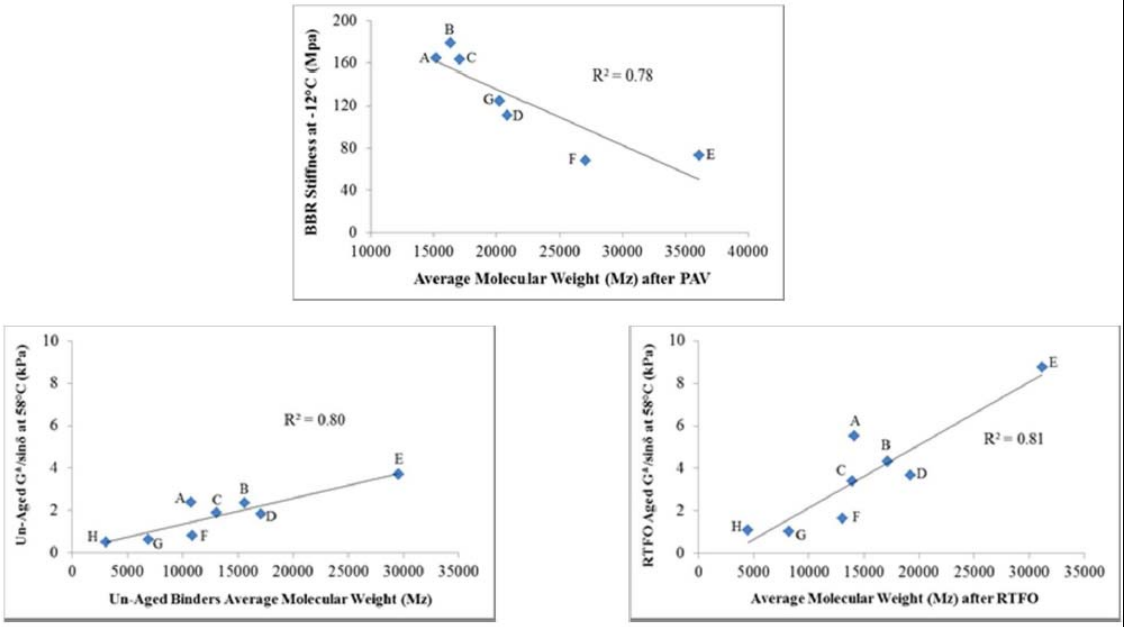


GPC

- Gel Permeation Chromatographic (GPC) is a method that has been used by different researchers to determine the definition of three classified groups in the binder, large (LMS), medium (MMS) and small molecular size (SMS);
- Aging results in a change in the molecular size distribution of an asphalt binder.
- Specifically, an increase in the large molecular size (LMS) results in an increase in the viscosity and stiffness of an asphalt binder.
- This viscosity change is predicted well by gel permeation chromatography (GPC)



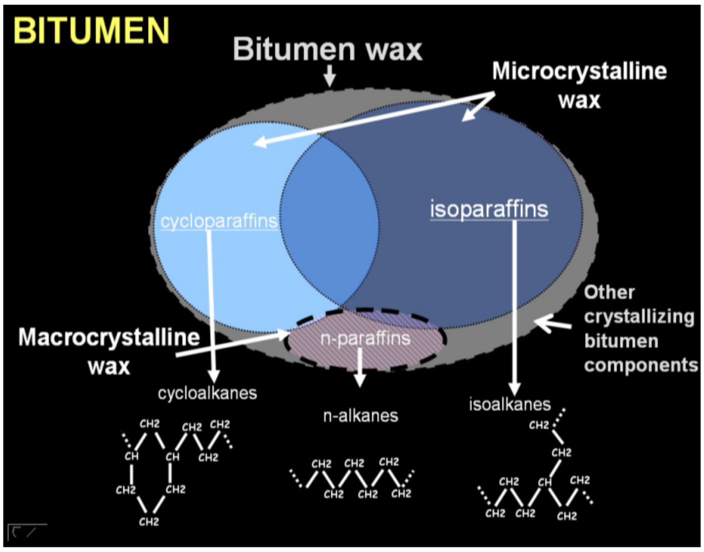
GPC enables also determine average molecular weight Mz



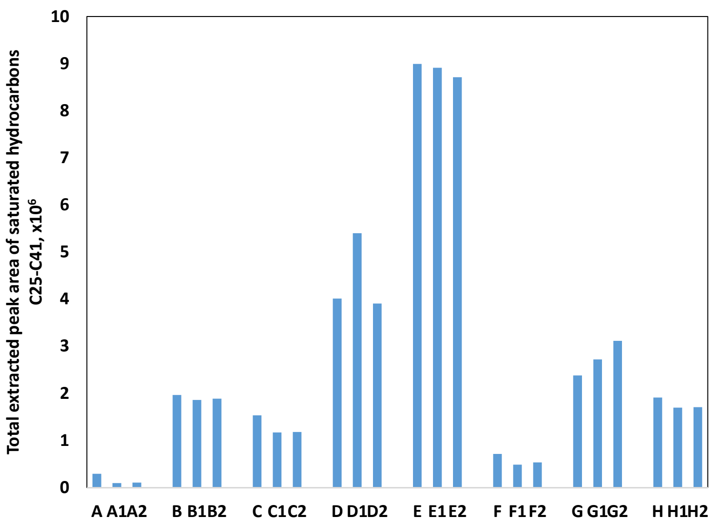
GC-MS

- Short- and long-chain hydrocarbons (n-alkanes)

- *There appear to be no binders with a high wax content and low grade loss. This provides indirect evidence that the amount of wax in the binder at room temperature is an indicator of the tendency for the material to reversibly age at lower temperatures. (Hesp et.al 2007)*



Picture: Ylva Edwards Ph.D thesis, KTH „Influence of Waxes on Bitumen and Asphalt Concrete Mixture Performance“



Yet to come

- SARA fractions
  - It is expected that a good balance exists between both the polar and the non-polar molecules in order for the asphalt to show good performance in service.
- Wax content with DSC and TGA
  - Some countries have set a limit to wax content. Can we see the relationship between wax % and behavior?
- Modification to meet PG and physical hardening requirements.
- DRS study what is happening with our bitumen on the road -> how fast is ageing?

Conclusions

- The study has not been finished yet, so final conclusions are coming later.
- According to PG and MSCR tests our bitumen HT is enough and studied bitumen are not the reason why we see ruts on our roads (if we exclude studded tires);
- Problem is LT and physical hardening, fatigue.

Suggestions for the future

- As AC consists bitumen, filler and aggregate and these have to work in synergy in order to have good pavement performance.
  - Bitumen is covered;
  - Mastics and asphalt mixtures has to be next.
- Moisture damage as the cause of raveling?
- Definitely some test sections are needed to validate the study results for our local conditions.

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Thanks!

References

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