AV '17 KONFERENCE ASFALTOVÉ VOZOVKY 2017

Better Polymer Modified Bitumen (PmB) via crosslinking

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ValoChem

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Motto: Asfaltové vozovky – bezpečná cesta k prosperitě

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EAPA

PRAGOPROJEKT

Agenda

I. Past and future needs for transportation

II. How PmB and crosslinking meet those needs

III. Case study : European tests

IV. Case study : US tests

V. Conclusions

I. **Past and future needs for transportation**

II. How PmB and crosslinking meet those needs

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Transportation evolution in Europe since 1995

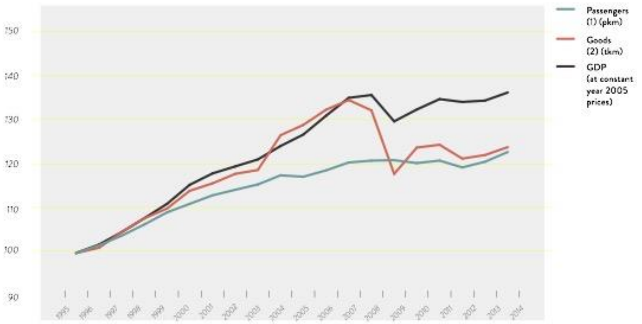
Traffic increase

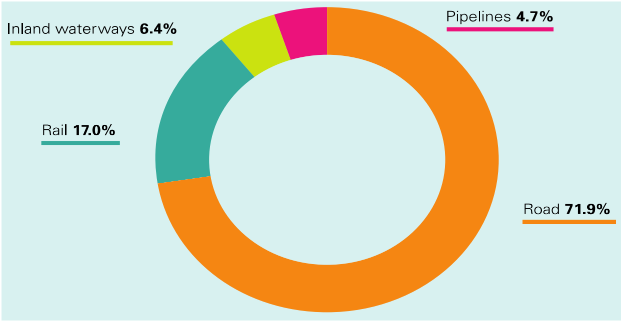
- **Since 1995 about 20% traffic increase**

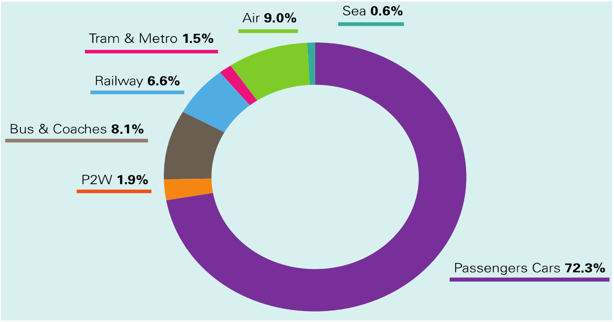
Split between transportation modes 1995 - 2013

- **72-73% by roads**
  - Goods: From 1300 to about 1700 billion t/km (+1.2% per year)
  - People: From 3800 to about 4500 people/km (+1.4% per year)
  - About 32% of the European turnover is generated by transports
- **17% by train**
- **other modes**

Transport growth in EU 28, evolution 1995-2014







Funding - Investment

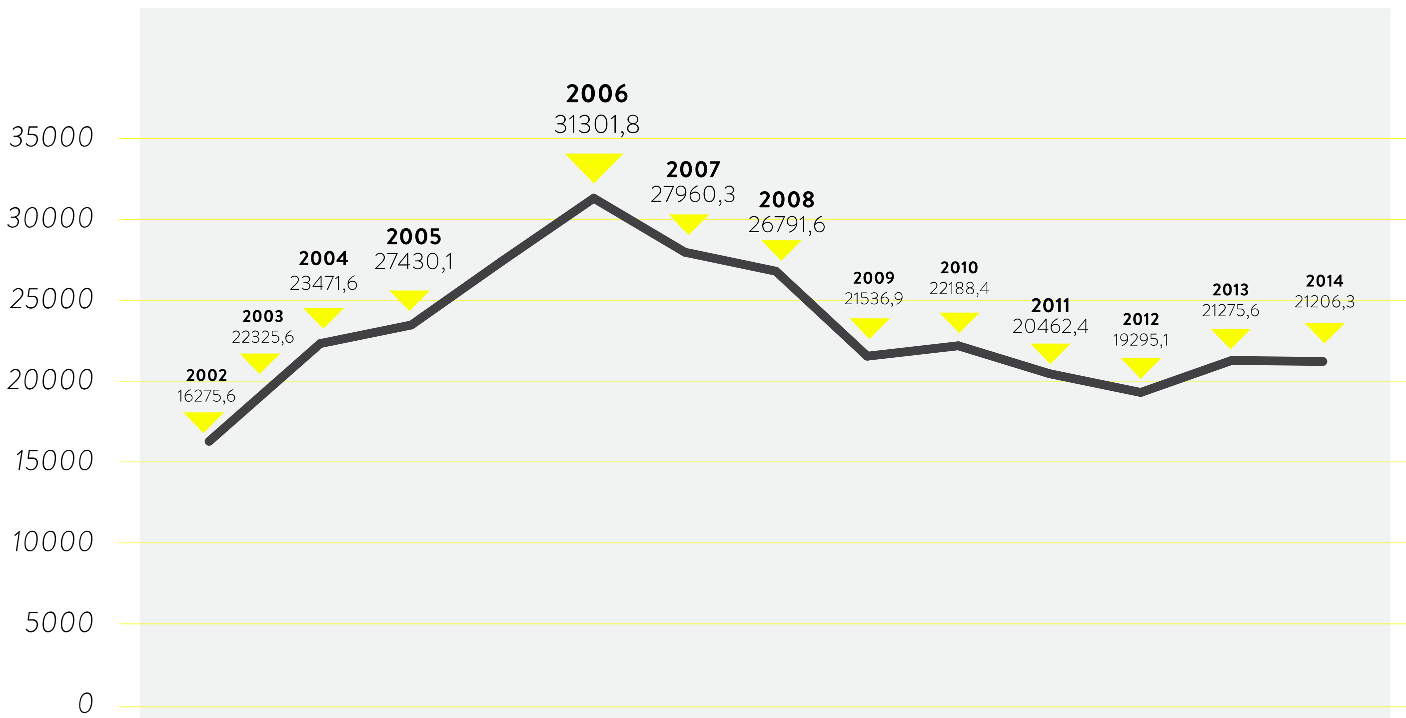
European Investment Bank Loans for Transport to EU 28, 2006-2015
(EUR million)

	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Roads, Motorways	4384	3542	4932	6030	3716	3876	2726	4728	5384	2827
Railways	2999	3534	2495	2704	4352	4624	3541	3419	3875	5548
Urban Transport	1294	1924	1981	3399	4151	4411	2655	2733	2865	3371
Air Transport	764	644	2458	1740	487	500	261	420	428	18
Maritime Transport	593	454	894	1.821	496	793	863	212	368	586
Intermodal Freight Terminals and Other Transport	36	29	763	n.a.	2	66	28	81	45	15 60
Total Transport Sector	10.070	10.127	13.523	15.694	13.204	14.270	10.074	11.593	12.965	12.425

- **Global decrease in road investment for the past 9 years (40% loss)**
- **Increase in railways and urban transportation mode**

Funding - Maintenance

Maintenance expenditures in road infrastructure in selected countries, 2002 - 2014 *(million Euros)*



- **Since 2006 global decrease of spending in road maintenance**
- **From 31.3 billion Euros in 2006 to 21.2 billion Euros in 2014**

Weather conditions – 1960 to 2015

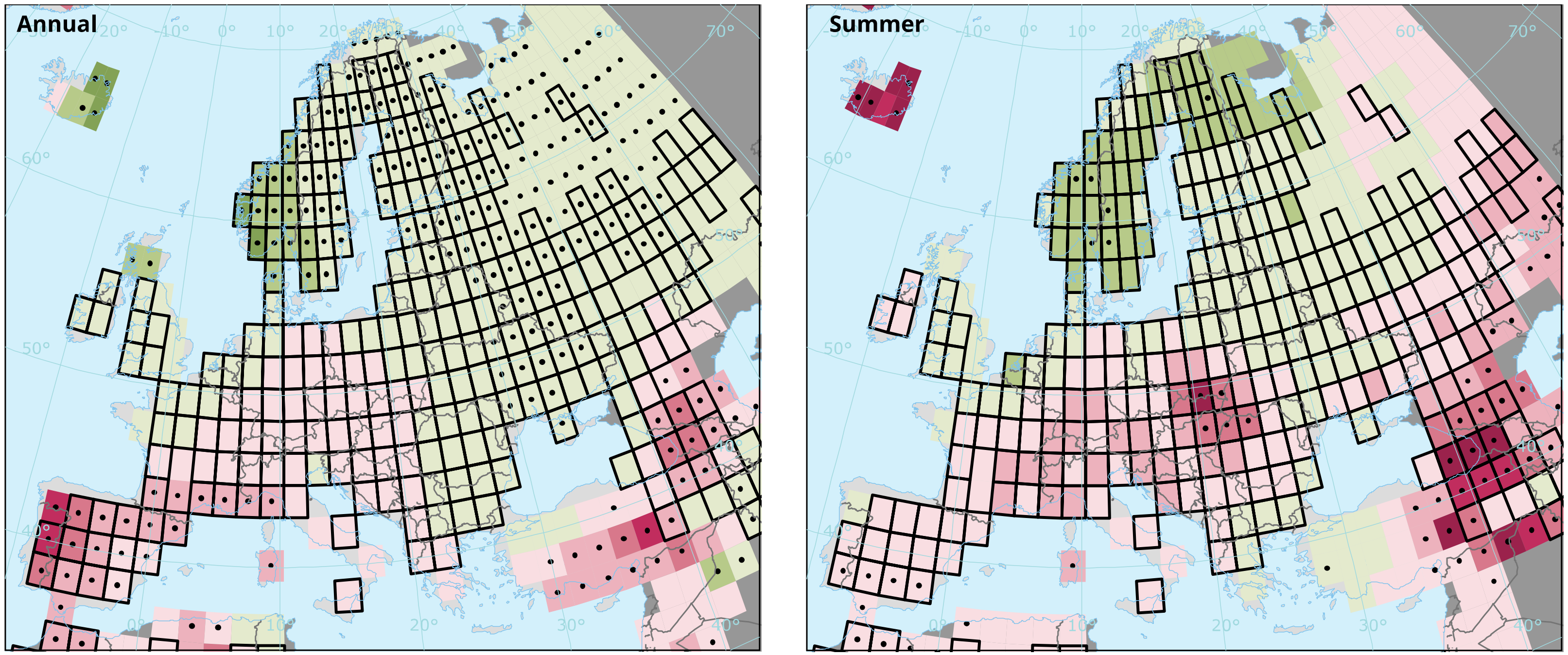
- **Western and southern European regions**
  - Decrease in global precipitations
  - Increase of average temperature

- **Northern and north-eastern European regions**
  - Increase in global precipitations as well as heavy rains
  - Global warming

« The WEATHER project estimated the costs of weather events for road transport to be roughly EUR 1.8 billion annually for 2000–2010. Infrastructure costs account for 53 % of those costs, followed by time costs (16 %) and health and life (accident-related) costs (13 %).
Costs would increase by 7 % by 2040–2050, mainly driven by higher infrastructure costs; in fact, the other components, related to users' costs and services, would decrease. This increase would not be homogeneous across Europe: the highest increases were estimated for France (72 %) and Scandinavia (22 %) (Enei et al., 2011) »

Extracted from 5.5.3 - Climate change impacts and vulnerabilities 2016 THAL17001ENN

Precipitations



Trends in annual (left) and summer (right) precipitation across Europe between 1960 and 2015

Annual precipitation (mm/decade)

– 80 – 60 – 40 – 20 0 20 40 60 80

0 500 1 000 1 500 km

Summer precipitation (mm/decade)

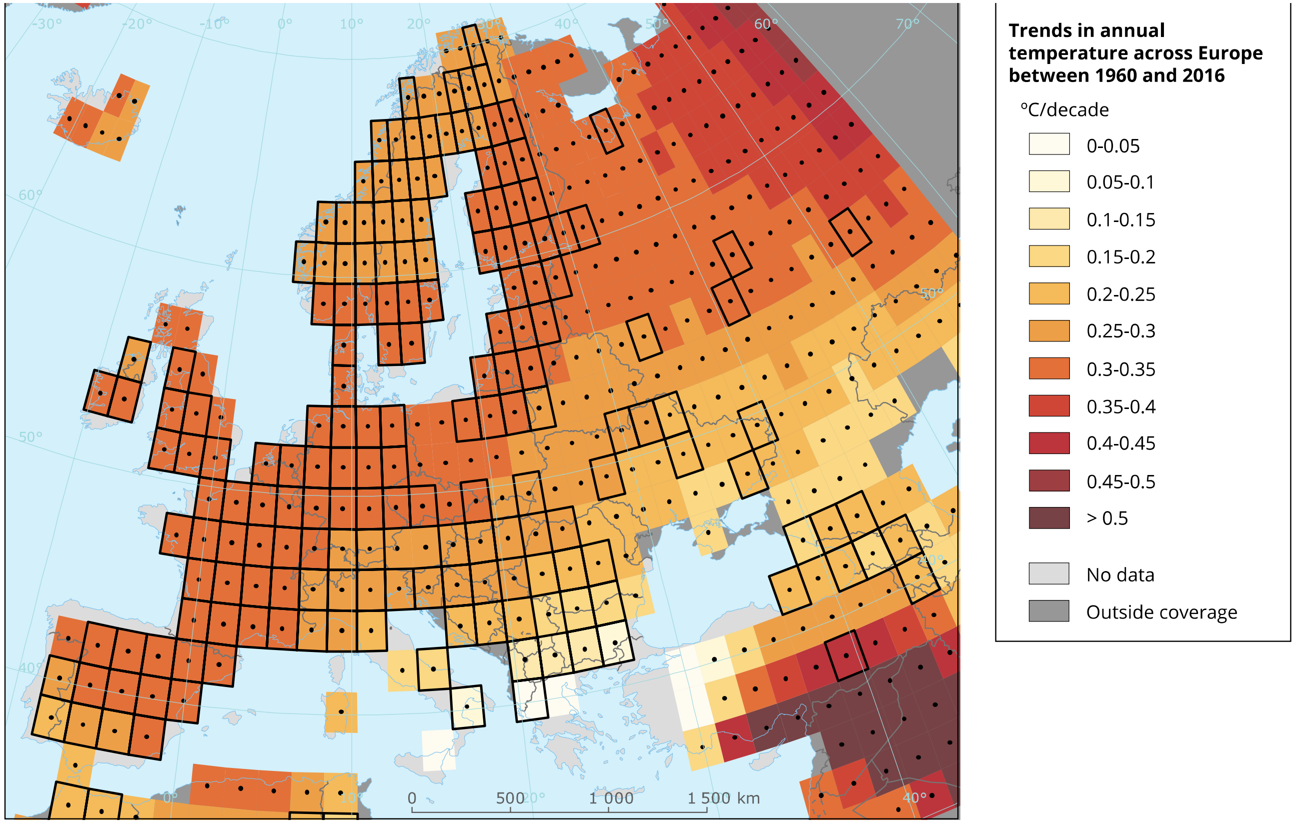
– 20 – 15 – 10 – 5 0 5 10 15 20

No data

Outside coverage

https://www.eea.europa.eu/data-and-maps/indicators/european-precipitation-2/assessment

Warming



https://www.eea.europa.eu/data-and-maps/figures/decadal-average-trends-in-mean-7

What do those figures say ?

More and more severe field constraints

- Increase of traffic volume with time
- Power steering, heavier weight and larger tires of vehicles

Funding

- Less and less money for investment and/or maintenance

Global warming

- Climate change (heavy rains and T°C increase)

What are the needs associated?

Improved performance of materials

- Better resistance to higher field constraints
- Adaptability to climate change

Higher durability

- Longer-lasting materials for lower overall budget (investment + maintenance)
- And with initial cost control

I. Past and future needs for transportation

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What is expected from polymer modification ?

- **Lower thermal susceptibility vs. standard bitumen**
- **Improvement of elongation**
- **Better visco-elastic properties**
- **Better global resistance against pavement distresses**
    - Rutting
    - Thermal cracking
    - Fatigue cracking
    - Aging
    - Stripping

Polymer modification is the right technology to meet challenges exposed

Key feature for PmB production :

Compatibility between Bitumen and Polymer

Options :

- Selection of the right bitumen base and specific polymer
- Polymer compatibilizer
- Crosslinker

What about cost ?

How to make this technology easier to use and/or cheaper ?

Crosslinking effect (X-linking)

Theory

- Creation of covalent bonds in-between polymer chains
- Coupling of polymer and bitumen through sulfide and/or polysulfide bonds

Impact on binder characteristics

- Improvement of PmB storage stability
- General improvement of binder rheology
- Increase of elastic recovery and softening point

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Physical blends vs. X-linking – Case Study

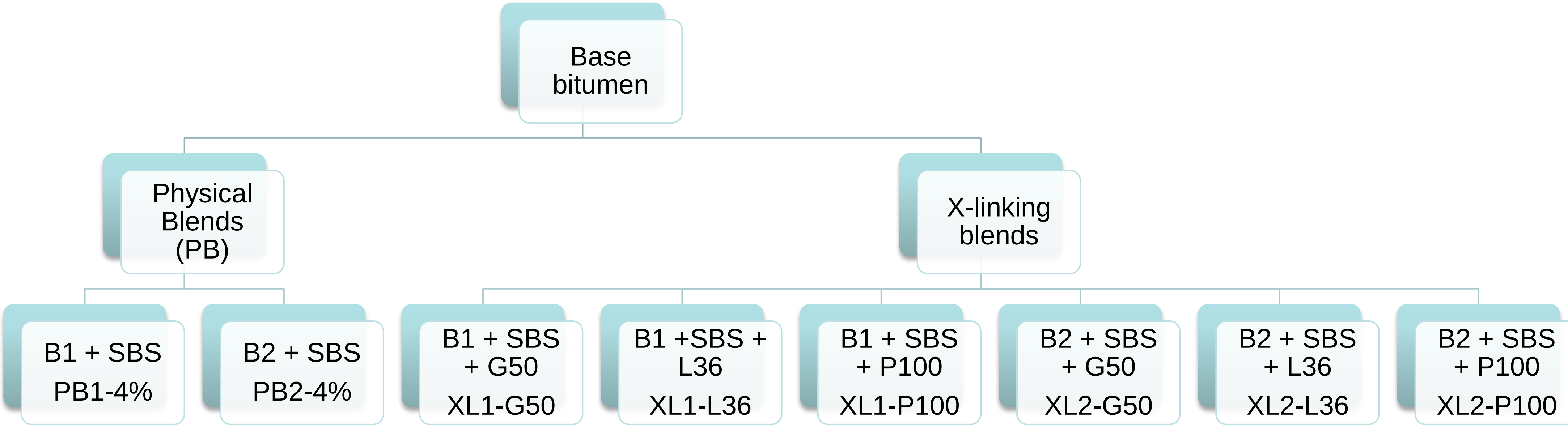
2 binders selected for their chemical differences:

	R&B SP (°C)	Pen 25°C (0,1mm)	SARA Analysis				Colloïdal index
			Saturates	Aromatics	Resins	Asphaltenes	
70/100 - B1	45,8	73	2,4	55,1	39,6	12,9	**0,16**
70/100 - B2	46,0	80	4,7	51,3	27,5	16,5	**0,27**

1 linear thermoplastic elastomer: SBS with 31% styrene

3 Crosslinking agents:

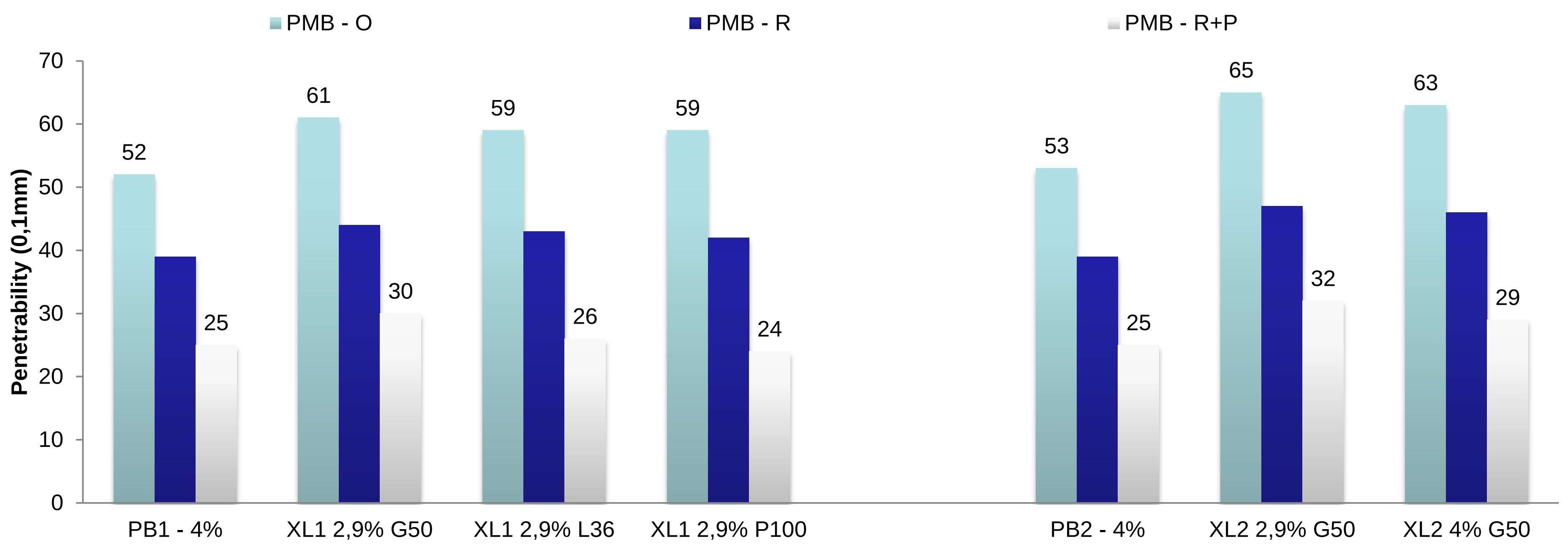
Crosslinkers	Aspect	H_2S Scavenger
G50	Grey granules	Yes
L36	Yellow liquid	No
P100	Yellow granules	No



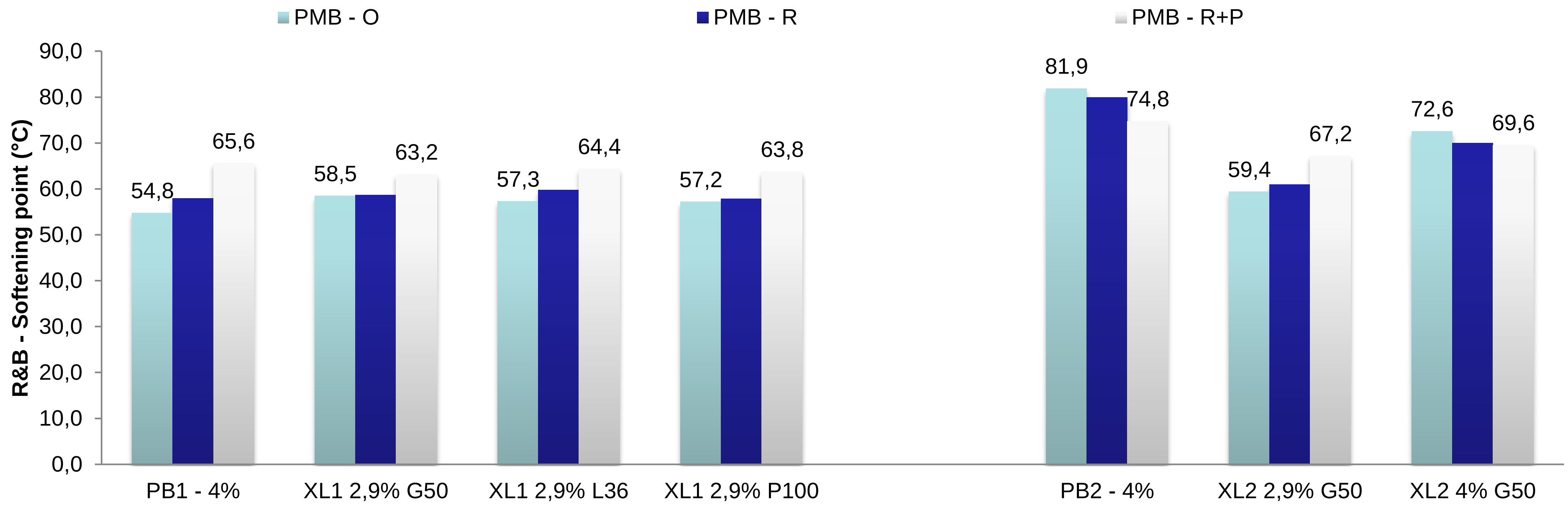
Manufacturing conditions:

- **Bitumen temperature: 180°C**
- **Mixing of bitumen + SBS: 30minutes @ 8000rpm**
- **When X-linking agent added, additional step of 15 minutes @ 8000rpm**
- **Stirring: 3 hours @ 800 rpm**
- **Maturation: 12 hours at 165°C**
- **Characterization**

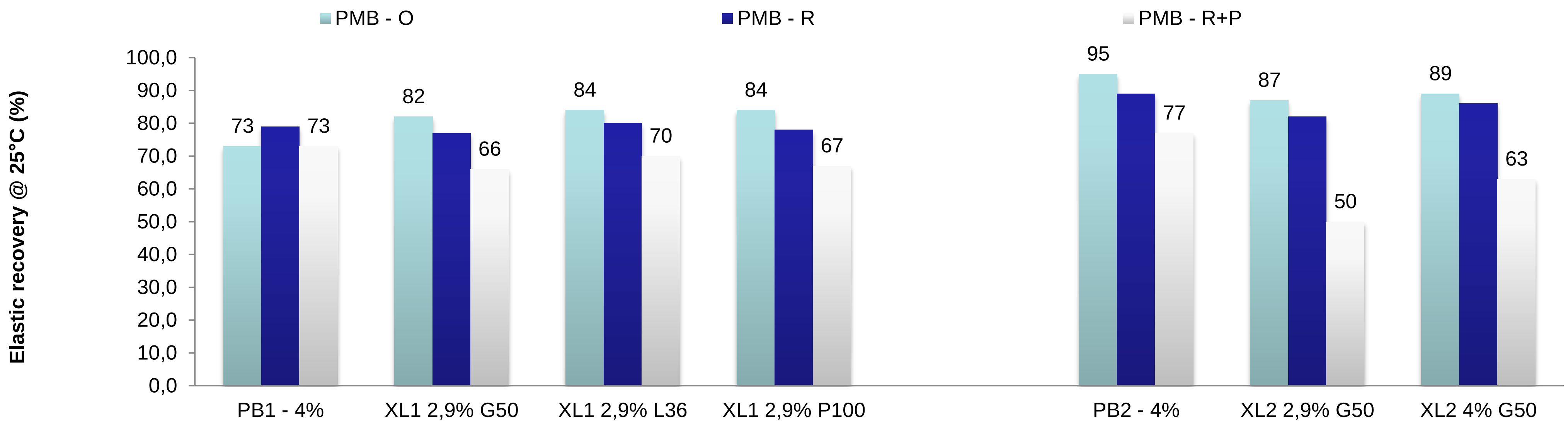
	PB 1 - 4%	XL 1 - 2,9%			PB 2 - 4%	XL 2 – 2,9%	XL 2 – 4%
	PB 1 - 4%	G50	L36	P100	PB 2 - 4%	G50	G50
Pen 25°C (0,1mm)	52	61	59	59	53	65	63
R&B – SP (°C)	54,8	58,5	57,3	57,2	81,9	59,4	72,6
ER @ 25°C (%)	73	82	84	84	95	87	89
Force ductility @ 5°C (J)	9,3	8,7	8,1	7,8	8,0	7,2	8,9
Storage stability Δ R&B – SP (°C) Δ Pen25 (0,1mm)	 -0,3 1	 0,0 2	 0,0 -5	 0,3 0	 1,9 2	 0,1 2	 2 -3
After RTFOT+PAV							
Pen 25°C (0,1mm)	25	30	26	24	25	32	29
R&B –SP (°C)	65,6	63,2	64,4	63,8	74,8	67,2	69,6
ER @ 25°C (%)	73	66	70	67	77	50	63
Force ductility @ 15°C (J)	5,1	1,5	4,0	2,4	3,7	-	5,2



- **B1 and B2 give similar trends when used in PmB formulations**
- **Difficult to have deeper analysis of binder performances when looking only at penetrability**



- **Strange reaction of B2 with 4% SBS**
  - High R&B but huge decrease after ageing (7°C loss)
  - B1 opposite trend, 11°C increase after ageing
- **Results obtained for PB2 seems overestimated**
  - Reaction of asphaltenes with SBS ?
  - Visbreaking residue ?



- **B1 more stable than XL1**
- **No real difference between the different XL1 binders**
- **Strange reaction of PB2 and XL2 with 4% SBS**
    - High ER but great decrease as well (18% and 26% loss after ageing)

First findings: European standards

Bitumen B1:

- X-linker keeps performances the same as physical blend whatever the ageing
- Questionable conclusion for Force Ductility on R+P aged binders
- Difficult to distinguish PmBs between each other
- X-linking allows significant reduction of SBS content to reach the same specifications: PMB cost is decreased

Bitumen B2:

- X-linking works differently than with B1
- Need to keep SBS content the same to match PB2 characteristics
- B2 bitumen is a difficult bitumen to use, not really compatible with polymer modification

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Characterization of binders based on US standards

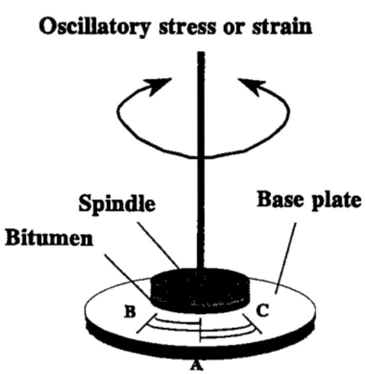
What if we look deeper into the PmB matrix ?

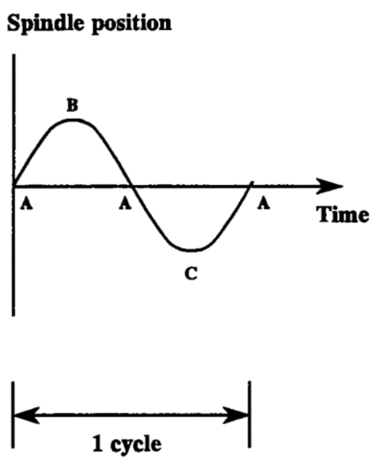
- PG Grading
- Multiple Stress Creep Recovery Test (MSCRT) (high, intermediate T°C)
- Bending Beam Rheometer (BBR) (low T°C)
- Epifluorescence Microscopy

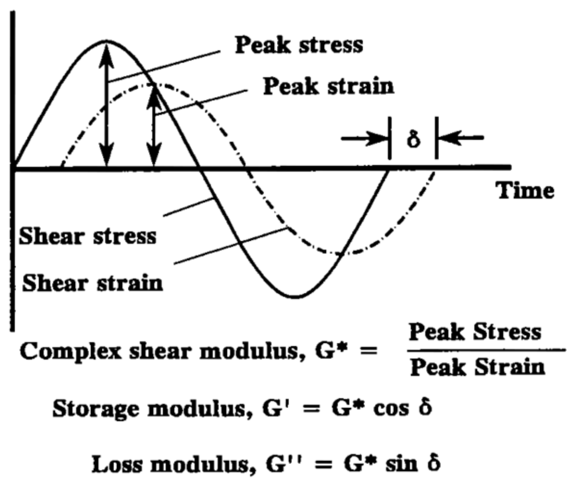
Dynamic shear Rheometer (DSR)

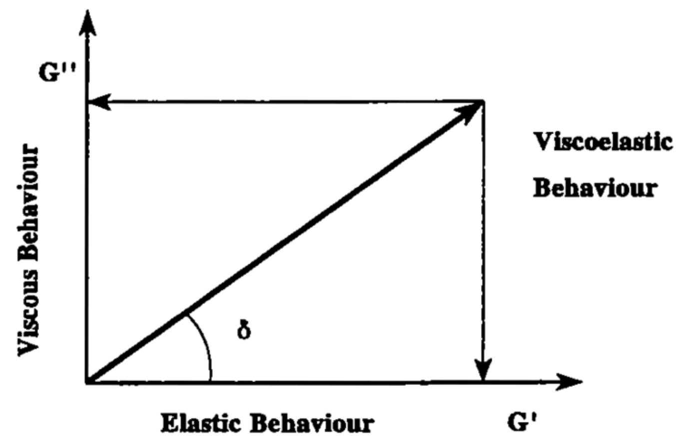
PG Grading

- G*/sin δ ≥ 1.00 kPa on fresh binder (rutting parameter)
- G*/sin δ ≥ 2.20 kPa on RTFOT aged binder (rutting parameter)
- G* sin δ ≤ 5000 kPa on RTFOT+PAV aged binder (intermediate temperature, fatigue parameter)
- BBR – low temperature determination









PG Grading

PG XX –YY (ZZ)

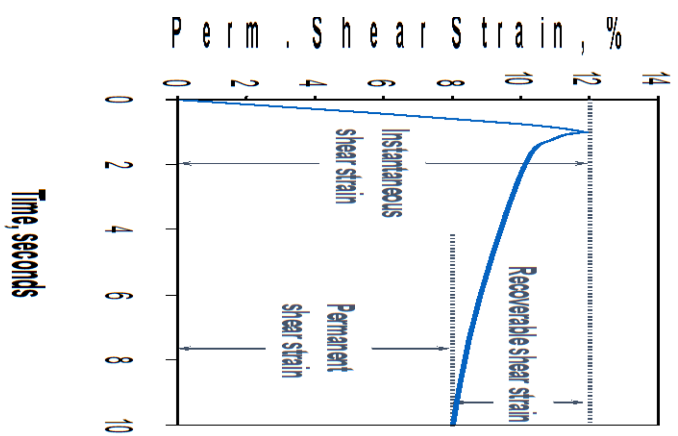
- XX: 7 days maximum pavement temperature
- YY: 1 day minimum pavement temperature
- ZZ: intermediate temperature test

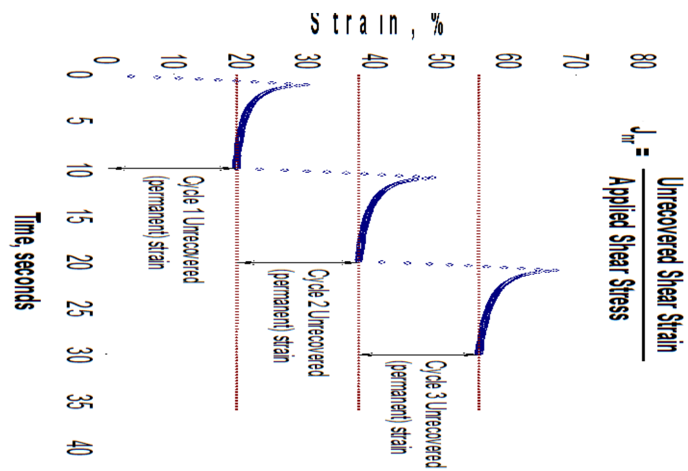
	PG Grade	Continuous PG Grade
PB1 – 4%	64 – 22 (25)	68.7 – 25.2 (24,9)
XL1 – 2,9% - G50	64 – 22 (25)	68.9 - 25.3 (22,8)
PB2 – 4%	76 – 16 (19)	78 – 21.5 (18,7)
XL2 – 2,9% - G50	64 – 22 (13)	66.8 – 25.9 (12,7)
XL2 – 4% - G50	70 – 28 (19)	74.2 – 28.8 (16,8)

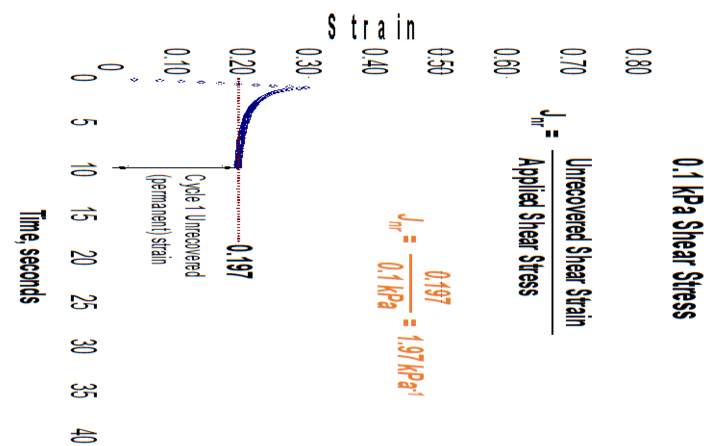
Multiple Stress Creep Recovery Test (MSCRT)

Part of the Superpave binder testing

- Test used to better describe stress dependency of binder, especially for PmB (improvement of initial SHRP Program)
- Selection of application temperature
- A shear stress is applied for 1s, then recovery is monitored for 9s (10x)
- Test performed at two different shear stress – 0.1kPa and 3.2 kPa



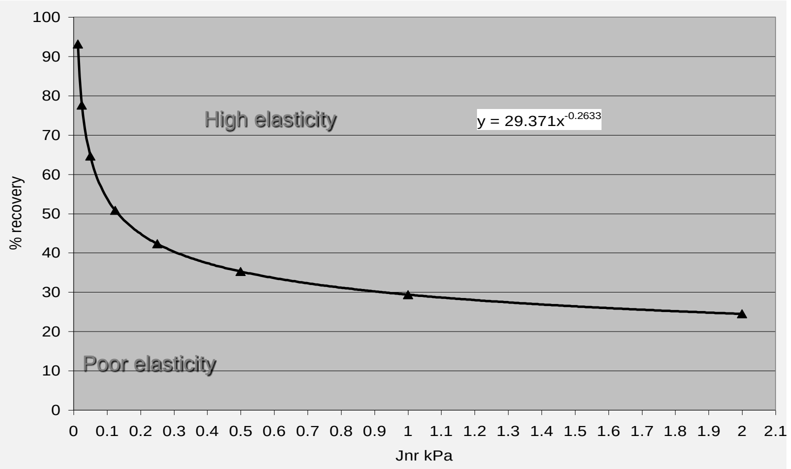




Multiple Stress Creep Recovery Test (MSCRT)

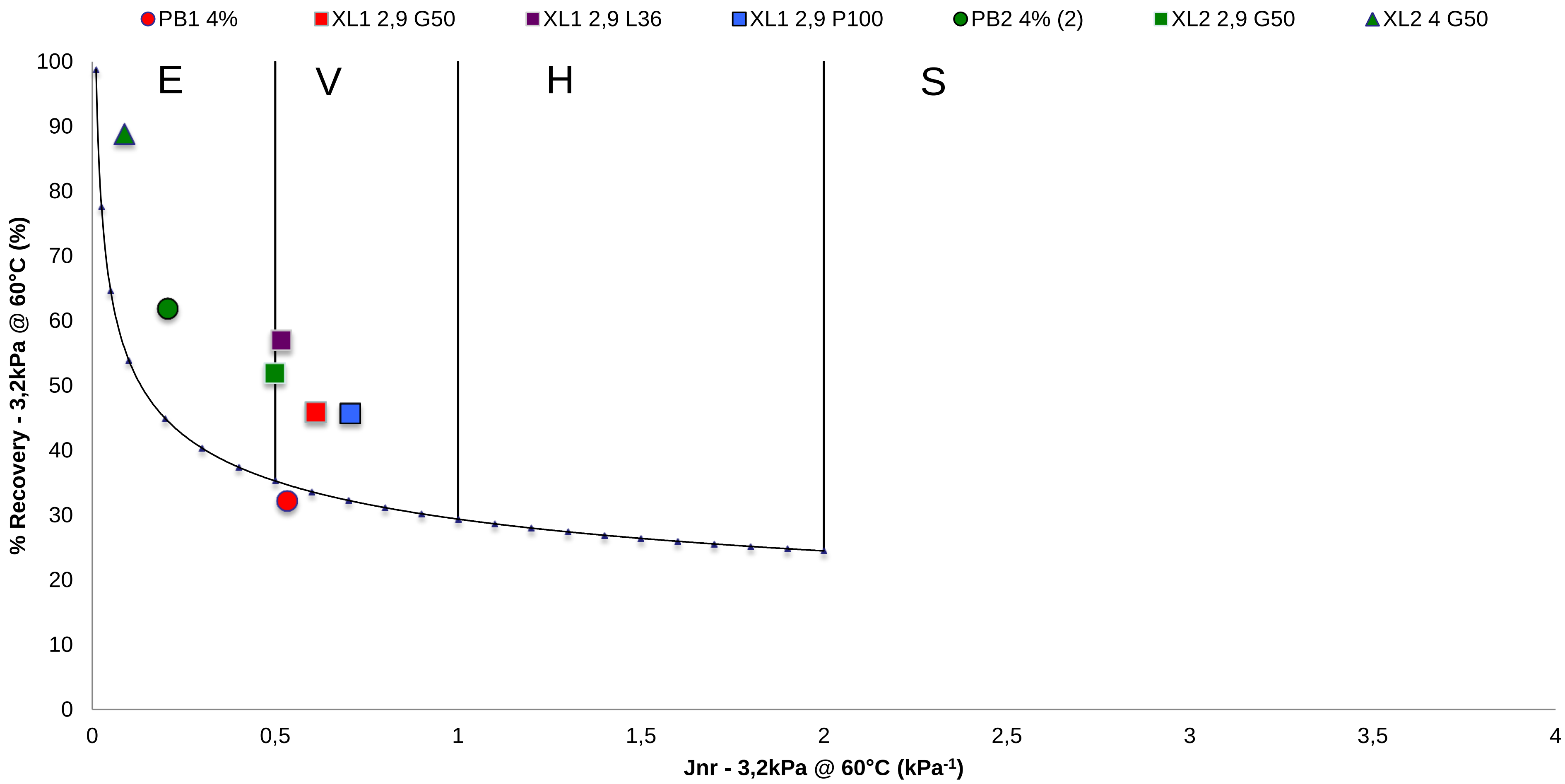
Information obtained

- Jnr: correlation with the T°C rutting
- Jnr-Diff: evaluation of the stress sensitivity of the binder (needs ≤ 75%)
- Percent recovery: validation of polymer modification



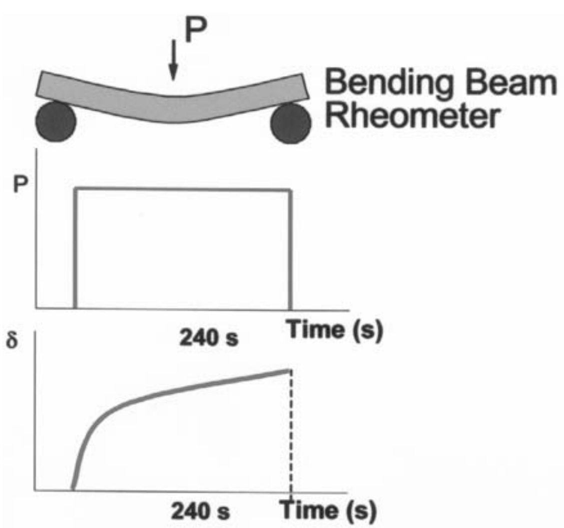
Traffic grading	ESALs	Traffic Load rate	Jnr limit
Standard - S-grade	< 10 million	> 70 km/h	≤ 4,5 kPa^{-1}
Heavy - H-grade	10-30 million	20 – 70 km/h	≤ 2,0 kPa^{-1}
Very Heavy - V-grade	> 30 milion	< 20km/h	≤ 1,0 kPa^{-1}
extreme - E-grade	> 30 milion	Standing	≤ 0,5 kPa^{-1}

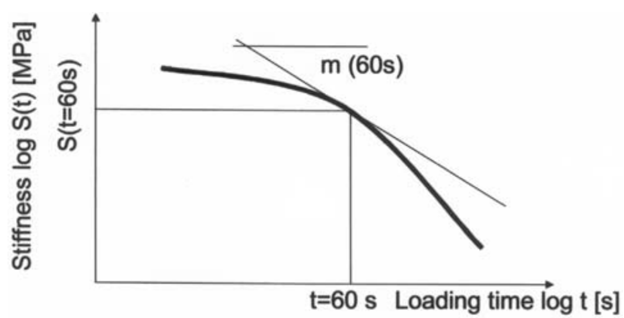
MSCRT on RTFOT aged binders

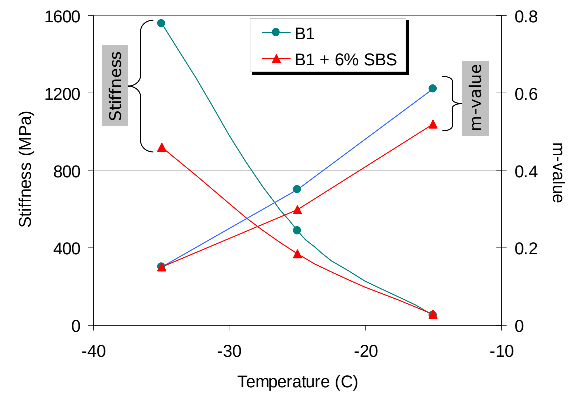


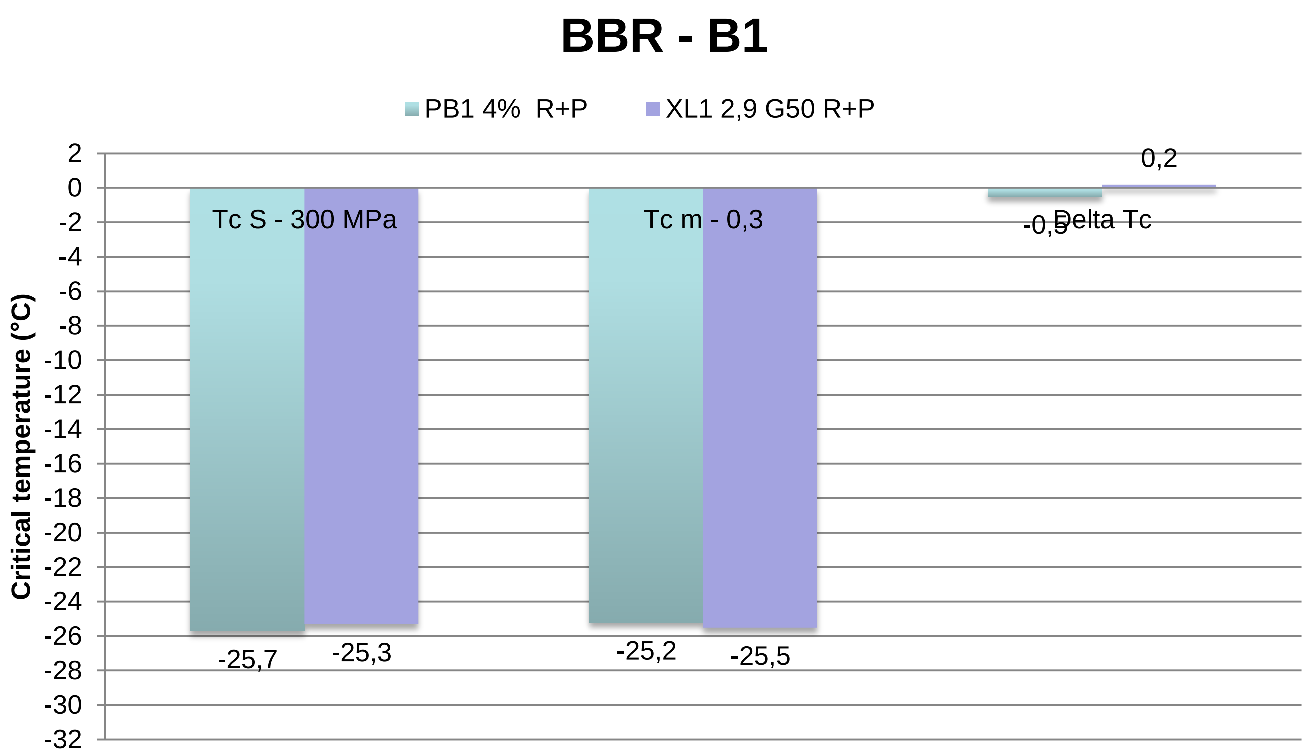
Bending Beam Rheometer (BBR)

- Measure of the low temperature stiffness modulus (S < 300MPa) and relaxation (m > 0.3 MPa) properties of a bituminous binder
- Indication of asphalt binder's ability to resist low temperature cracking
- ΔTc parameter = Tc S – Tc m gives sensitivity of the binder. Stiffness oriented binder or relaxation oriented binder









- PB1 and XL1 G50 have similar S and M values
- Positive ΔTc for XL1 G50, so more prone to relaxation
- Difficult to differentiate both binders, while XL1 contains 1.1% less SBS

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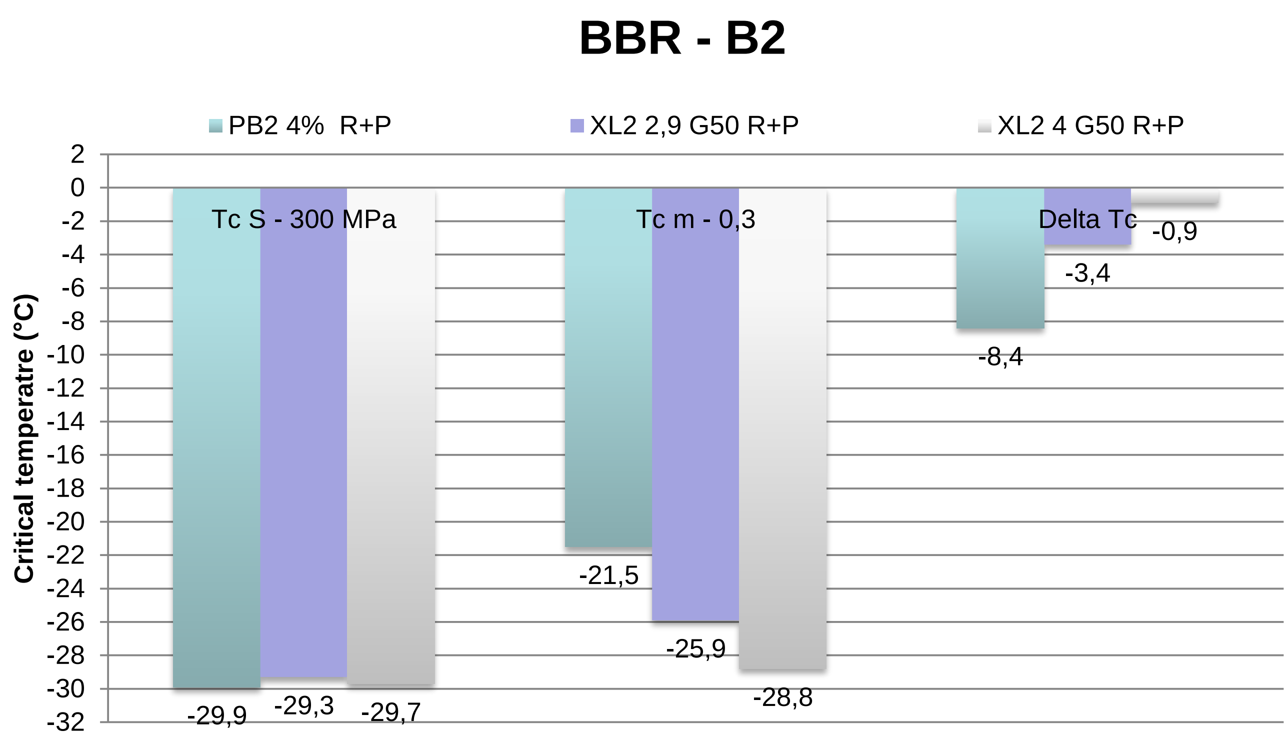
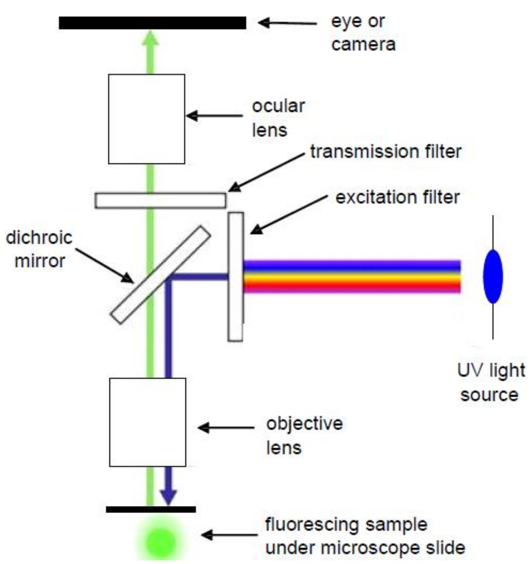
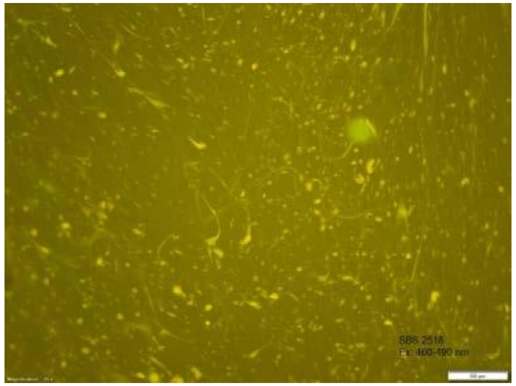


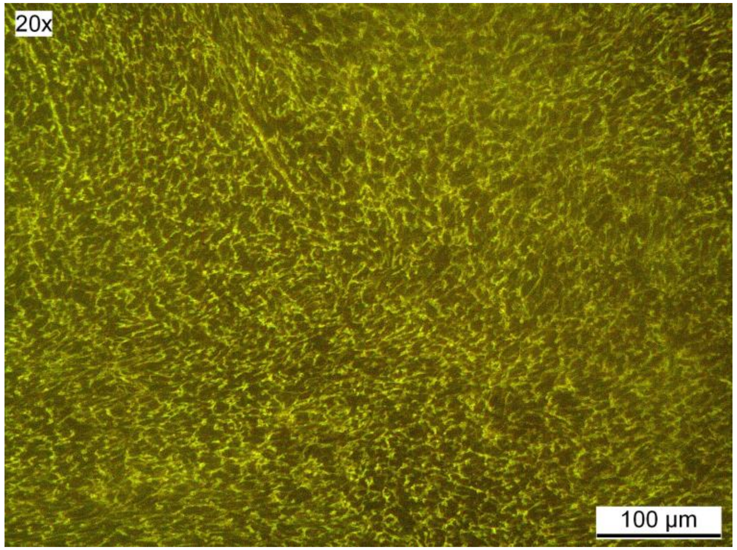
- PB2 is a S controlled binder, with bad ΔTc
- XL2 2.9 G50 is better due to better relaxation
- XL 4 G50 is definitely better, even if still S controlled

Epifluorescence Microscopy

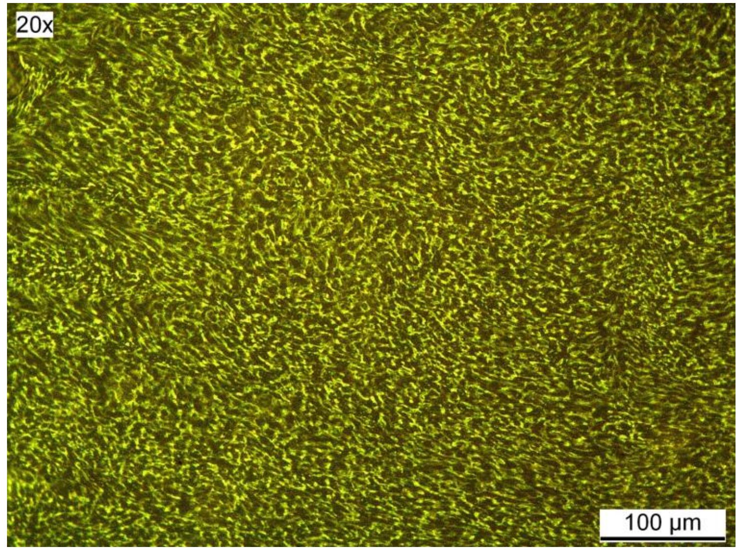




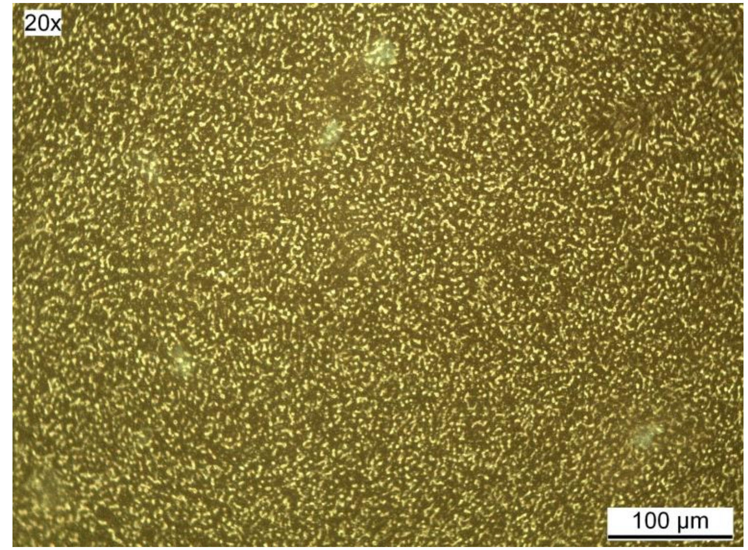
PB2 4% - O



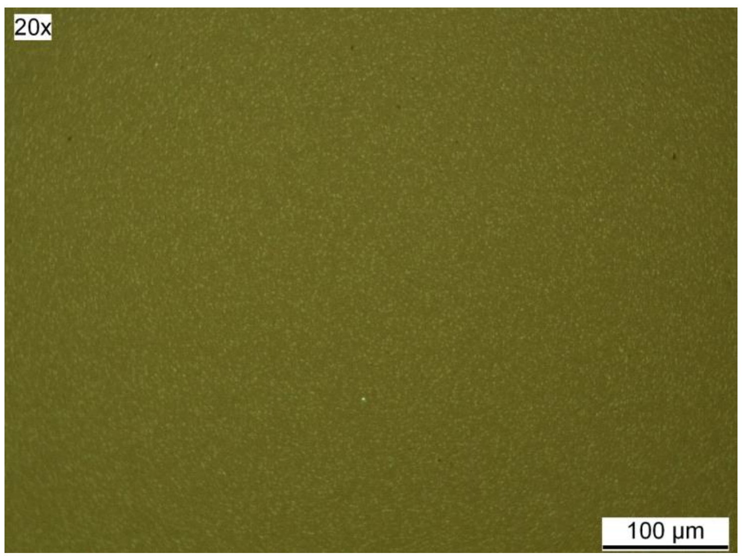
PB2 4% - R



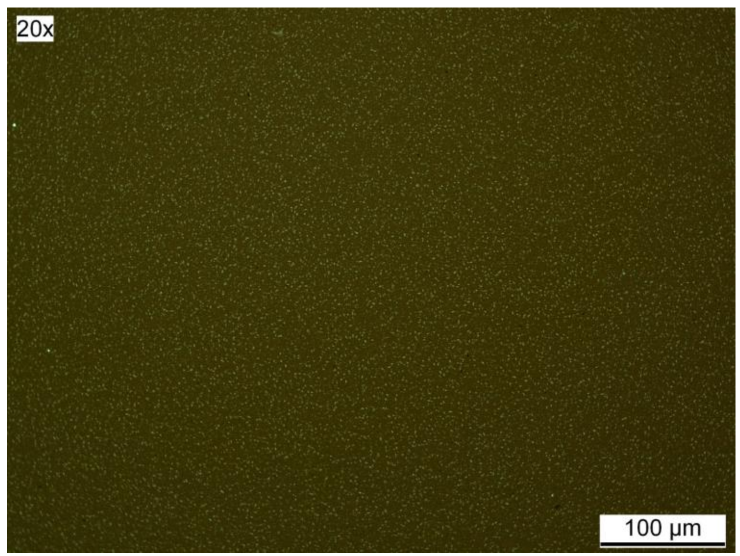
PB2 4% - R+P



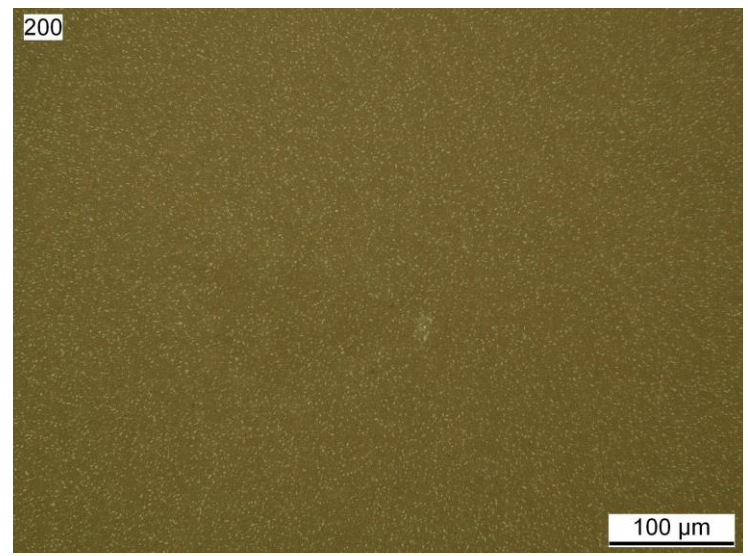
XL2 4% G50 - O



XL2 4% G50 - R



XL2 4% G50 – R+P



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Conclusion

Bitumen B1:

- X-linker keeps performances at the same level as physical blend whatever the ageing
- But questionable conclusion for the force ductility of R+P aged binders
- Difficult to distinguish PmBs between each other
- **X-linking allows significant reduction of SBS content to reach the same specifications: PmB cost is decreased**

Bitumen B2:

- X-linking allows usage of this bitumen for PmB production
- X-linker is a cost reducer that allows drastic improvement of bad bitumens

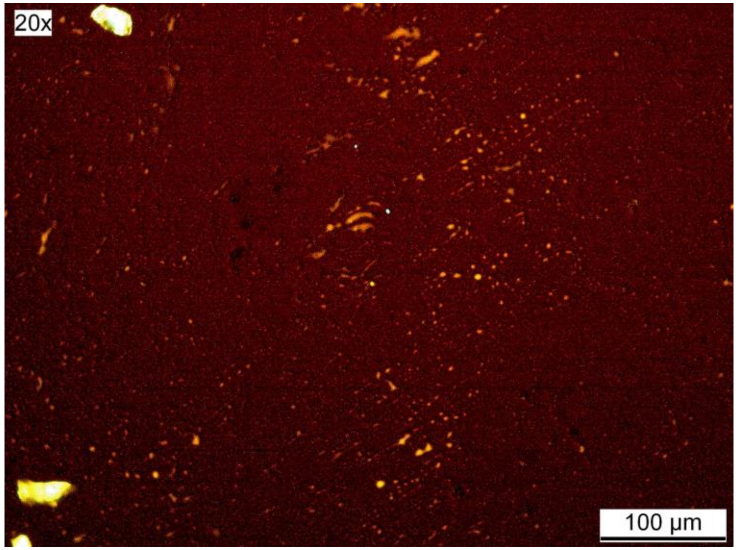
Thank You for your attention

Any question ?

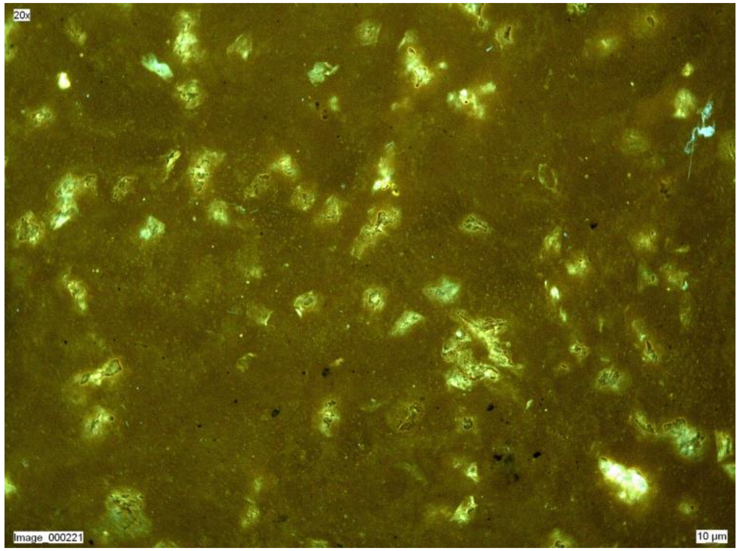
ValoChem

Valorization of Chemicals

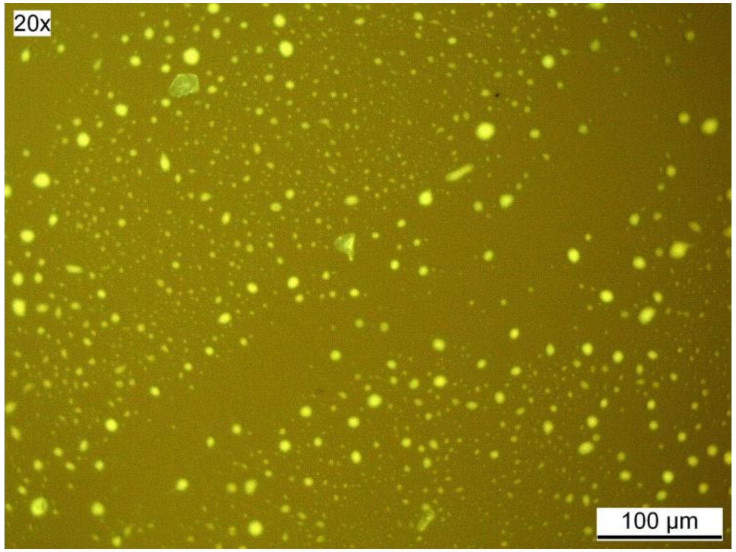
PB1 4% - O



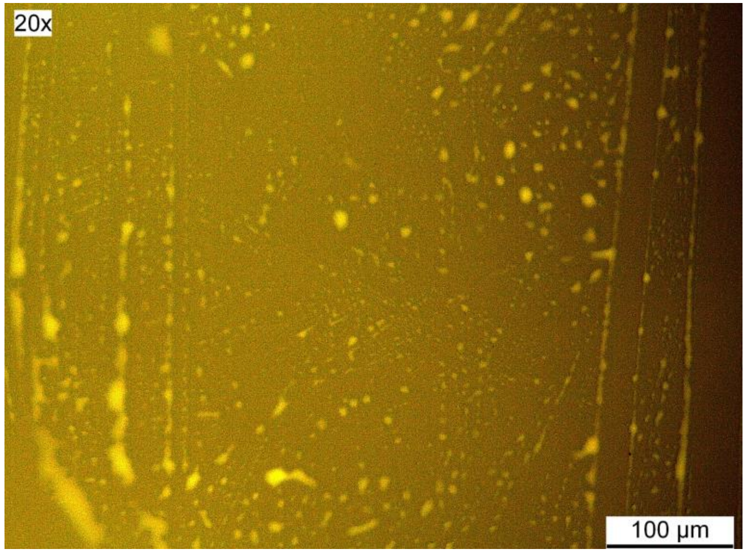
XL1 G50 - O



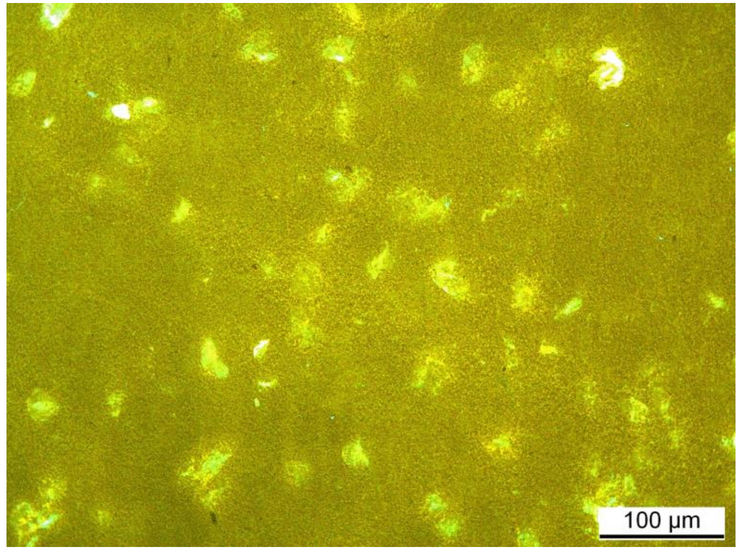
XL1 L36 - O



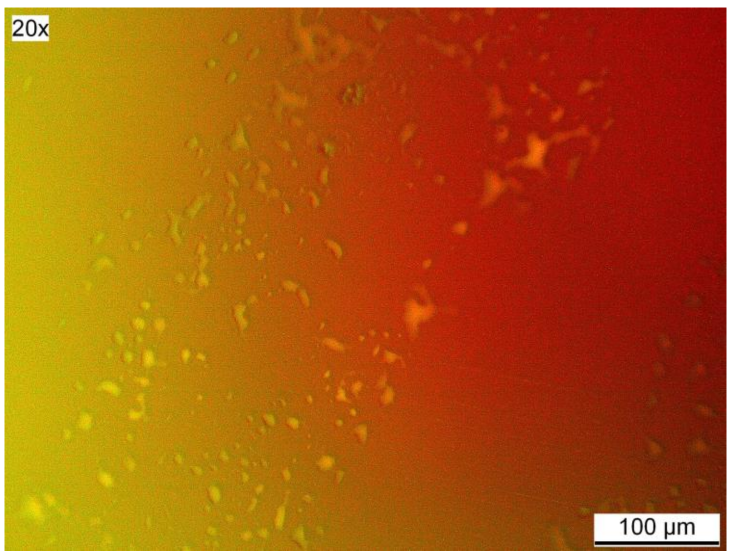
XL1 P100 - O



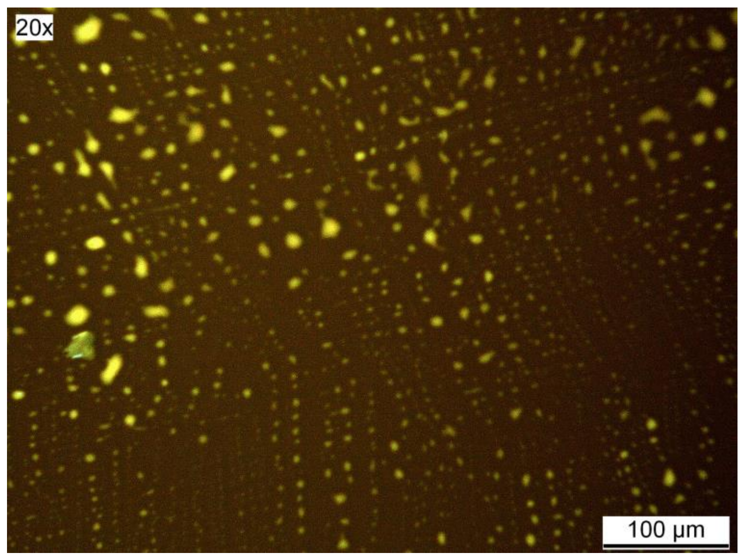
PB1 4% - R



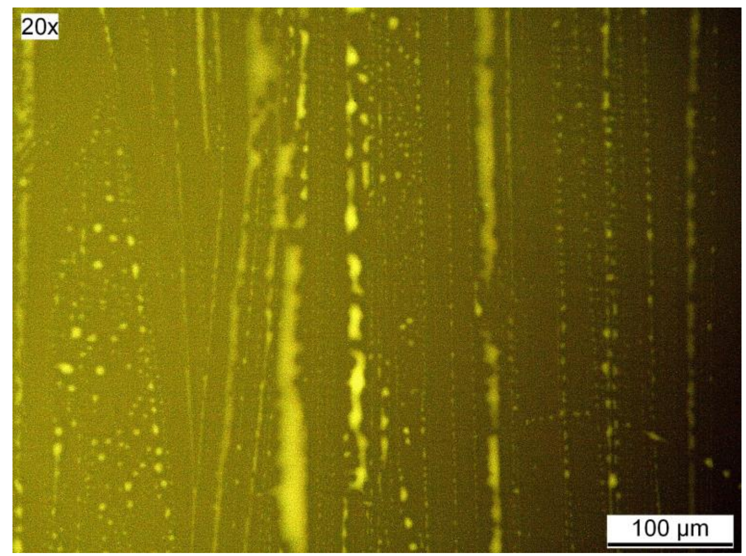
XL1 G50 - R

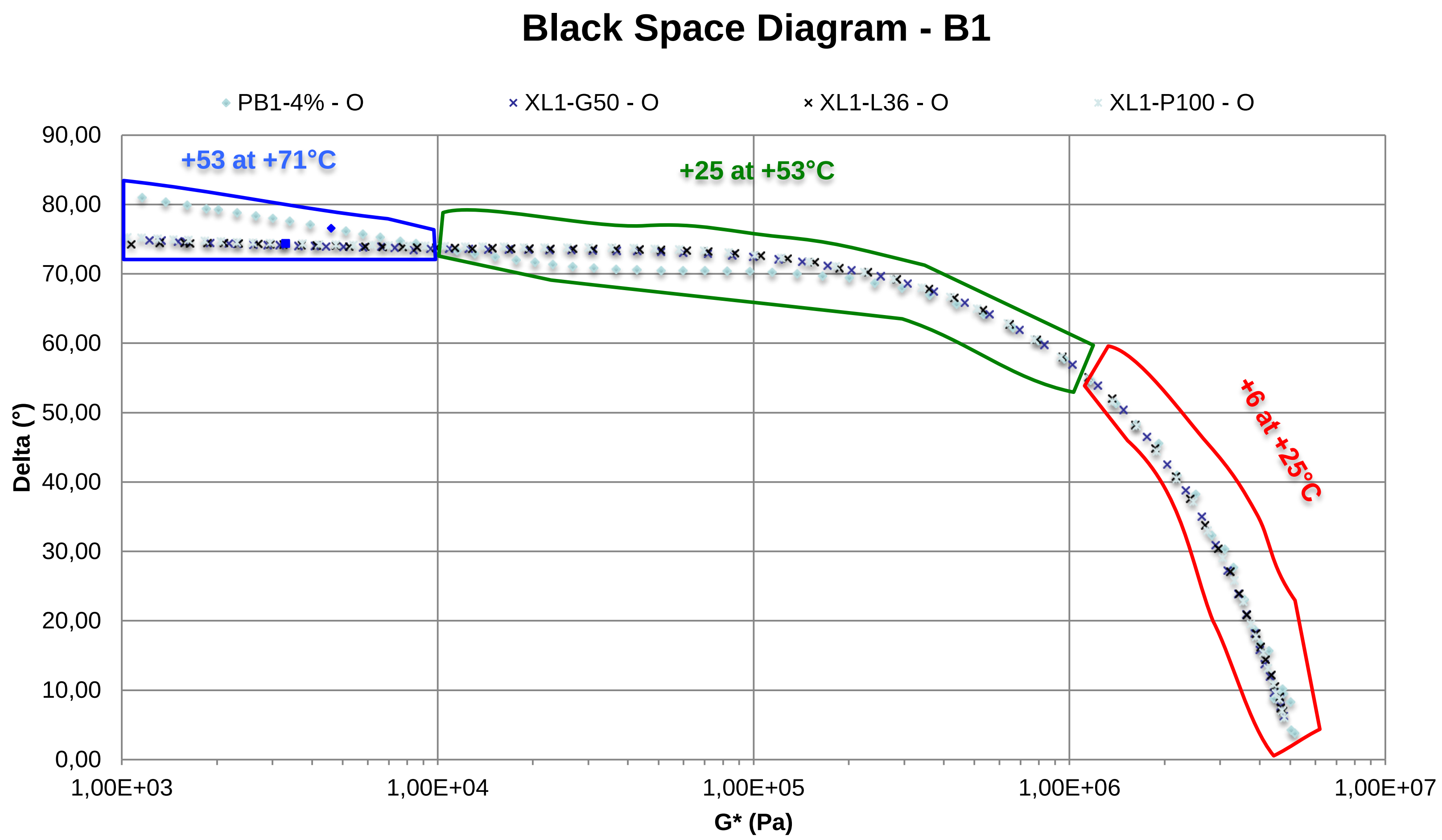


XL1 L36 - R

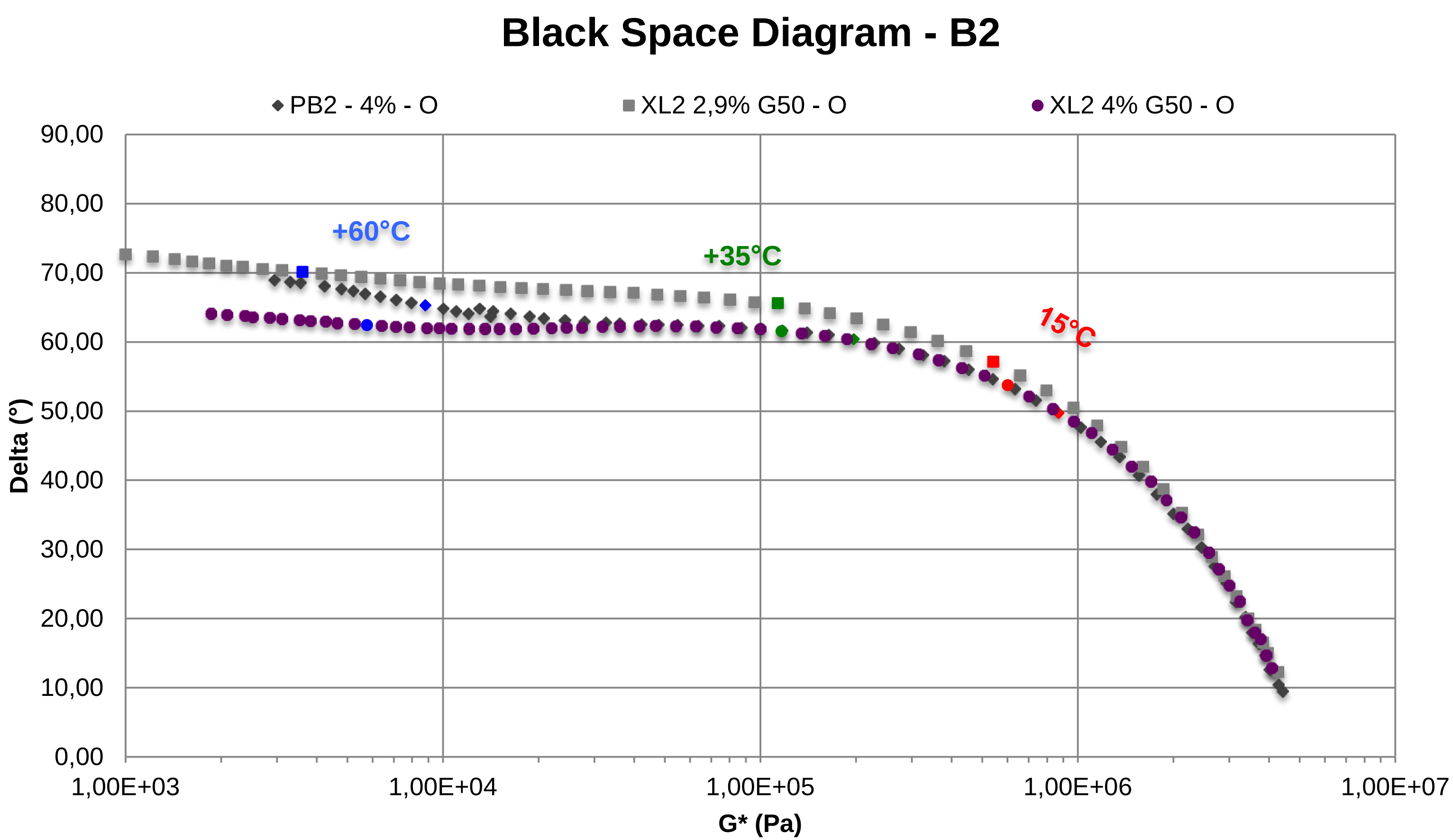


XL1 P100 - R





- PB1 is thermal sensitive at high T°C
- At high T°C PB1 behaves more like a viscous liquid – rutting ?



- **At low T°C PB2 is stiffer than XL2 2.9% and XL2.4%**
- **XL2 shows a lower thermal sensitivity than PB2**
  - Constant δ vs. T°C between 35 and 60°C