Glass Transitions in Complex Bituminous Binders [PPT]

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RILEM TC 272 PIM TG1 : Glass Transitions in Complex Bituminous Binders

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The RILEM TC 272 PIM (Phase and Interphase behaviour of innovative bituminous Materials) – TG1 Binder has initiated an inter-laboratory program investigating the phase and interphase behaviour of bituminous binders. Five laboratories evaluated the low temperature properties of seven standard and complex binders with differential scanning calorimetry (DSC). DSC has been accepted as a powerful tool to evaluate, among others, the glass transitions, T_g, monitoring the endothermic or exothermic heat flow of a material under controlled temperature conditions. There are different ways to run the test, conventional temperature linear-DSC (TL-DSC), and temperature modulation-DSC (TM-DSC). The latter has been proven as an efficient method differentiating the structural relaxation phenomena from the heat capacity. In this study, emphasis was laid on comparing the T_g measured by TL- and TM-DSC improving the interpretation of binder glass transitions. To restrain the scope of this study, two SBS polymer modified binders (PmBs), a commercially available PmB and an highly modified PmB (7.5 % SBS) , were evaluated and compared with two neat bituminous binders. It was observed that the modification by 7.5% SBS resulted in a decrease of the T_g. This reduction of T_g reflects the positive influence of SBS at low temperatures.

RILEM TC 272 PIM TG1
Glass Transitions in Complex Bituminous Binders

In 2020 Petersen Asphalt Research Conference

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The RILEM PIM

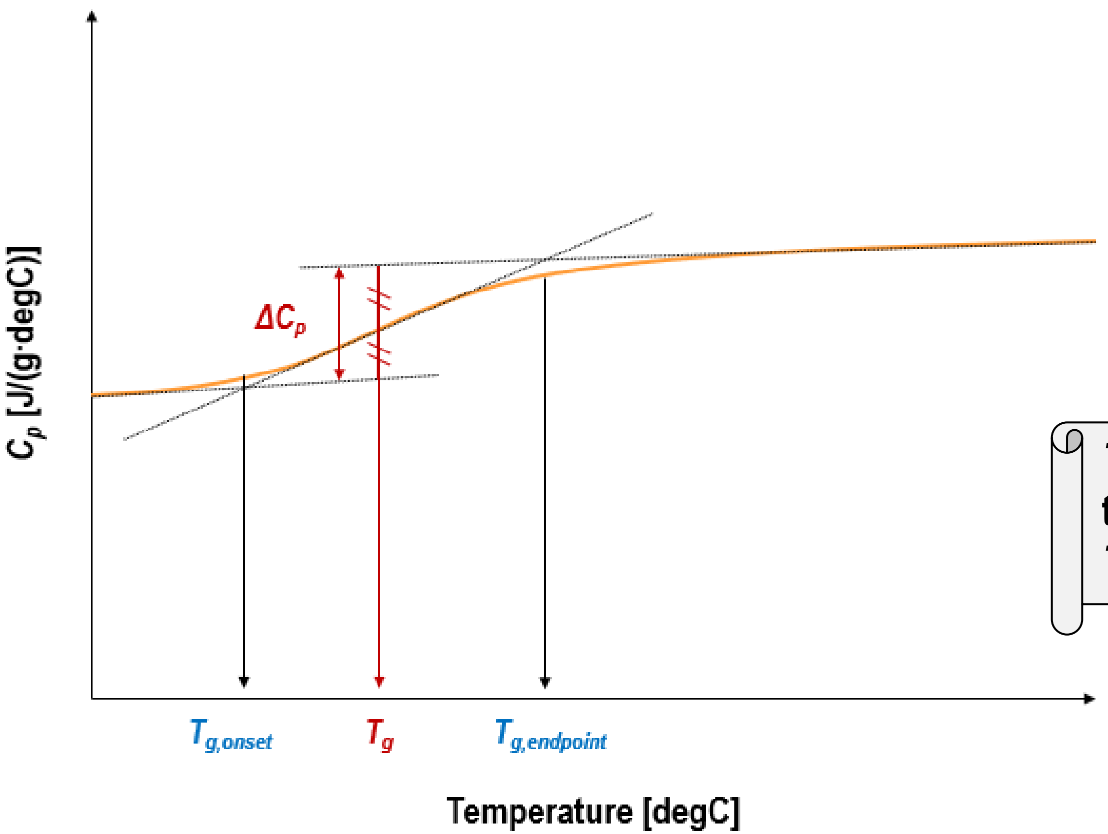
Rilem TC 272 - **P**hase and **I**nterphase in bituminous **M**aterials

- TG1 is about testing of complex bituminous binders
  - 17 labs participating from Europe and US
- Experiments
  - Physical properties and chemical structure
  - In a wide range of conditions

	Label	Description
Group 1	Bit1	Straight run bitumen 35/50 source Europe
	PmB1	Commercial Polymer modified Bitumen as for TG2
	PmB2	Lab made highly modified bitumen with 7.5 % SBS (HiMA)
Group 2	Bit2	Straight run bitumen 70/100 source Europe
	Blend1	*Bit1 + asphalt reuse additive as for TC RAP TG3*
	Blend2	*Bit1 + REOB*
	Blend3	*Bit1 + paraffinic oil*

Glass transition in binders

- Binders behave as glassy materials below the glass transition temperature (T_g), while above the T_g they behave as amorphous.
- The glass transition region is the temperature range that corresponds to the glass-to-amorphous transition. For binders, this region is between -50 and 0°C.
- The glass transition can assist on understanding the thermal cracking of binders.



T_g : the half-height between the heat capacity (C_p) of $T_{g,onset}$ & $T_{g,endpoint}$

Differential scanning calorimetry (DSC)

DSC measures the differences in heat flow [mW=mJ/sec] into a substance and a reference as a function of time and temperature, under a controlled temperature program.

$$\frac{dH}{dt} = \text{DSC heat flow signal}$$

$$\begin{aligned} Cp &= \text{Sample Heat Capacity} \\ &= \text{Sample Specific Heat x Sample Weight} \end{aligned}$$

$$\frac{dH}{dt} = Cp\frac{dT}{dt} + f(T, t)$$

$$\frac{dT}{dt} = \text{Heating Rate}$$

$$\begin{aligned} f(T, t) &= \text{Heat flow that is function of time} \\ &\quad \text{at an absolute temperature (kinetic)} \end{aligned}$$

Differential scanning calorimetry (DSC)

DSC measures the differences in heat flow (mW=mJ/sec) into a substance and a reference as a function of time and temperature, under a controlled temperature program.

- When measuring the T_g, the molecular motion associated with the glass transitions is time dependent. The T_g increases when heating rate increases in DSC
- When reporting the T_g, it is necessary to state the experimental conditions (heating rate, sample size, etc.) and how the T_g is determined

Different laboratories

Lab1
TL-DSC:protocol1

1	Isothermal | 165 degC	for 5 min
2	Non-isothermal | 2 degC/min	to -60 degC
3	Isothermal | -60 degC	for 5 min
4	Non-isothermal | 2 degC/min	to 165 degC

DSC Q2000, TA

Lab2
TM-DSC:protocol1

1	Isothermal | 165 degC	for 5 min
2	Non-isothermal | 5 degC/min	to -90 degC
3	Isothermal | -90 degC	for 5 min
4	Modulationl | 10 degC/min	0.5 degC for 80 sec to 165 degC
5	Isothermal | 165 degC	for 5 min
6	Non-isothermal | 2 degC/min	to -90 degC
7	Isothermal | -90 degC	for 5 min
8	Non-isothermal | 2 degC/min	to 165 degC

DSC Q2000, TA

Lab5
TM-DSC:protocol2

1	Isothermal | 165 degC	for 5 min
2	Modulation | 2 degC/min	0.5 degC for 60 sec to -60 degC
3	Isothermal | -60 degC	for 5 min
4	Modulation | 2 degC/min	0.5 degC for 60 sec to -60 degC

DSC 6000, PerkinElmer

Lab12
TL-DSC:protocol2

1	Isothermal | 25 degC	
2	Non-isothermal | 20 degC/min	to 130 degC
3	Isothermal | 130 degC	for 1 min
4	Non-isothermal | 10 degC/min	to -80 degC
5	Isothermal | -80 degC	for 1 min
6	Non-isothermal | 10 degC/min	to 160 degC
7	Isothermal | 160 degC	for 1 min
8	Non-isothermal | 10 degC/min	to -80 degC
9	Isothermal | -80 degC	for 1 min
10	Non-isothermal | 10 degC/min	to 0 degC
11	Isothermal | 0 degC	for 5 min
12	Non-isothermal | 10 degC/min	to -80 degC
13	Isothermal | -80 degC	for 1 min
14	Non-isothermal | 20 degC/min	to 160 degC

DSC2 STARe with M-DSC TOPEM, Mettler Toledo

Different labs - Different protocols

Temperature-Linear (TL-DSC)

Temperature-Modulation (TM-DSC)

Binders

To restrain the scope of this study, 4 binders were evaluated :

Bit1 – 35/50 penetration graded bituminous binder [PG 70-22]

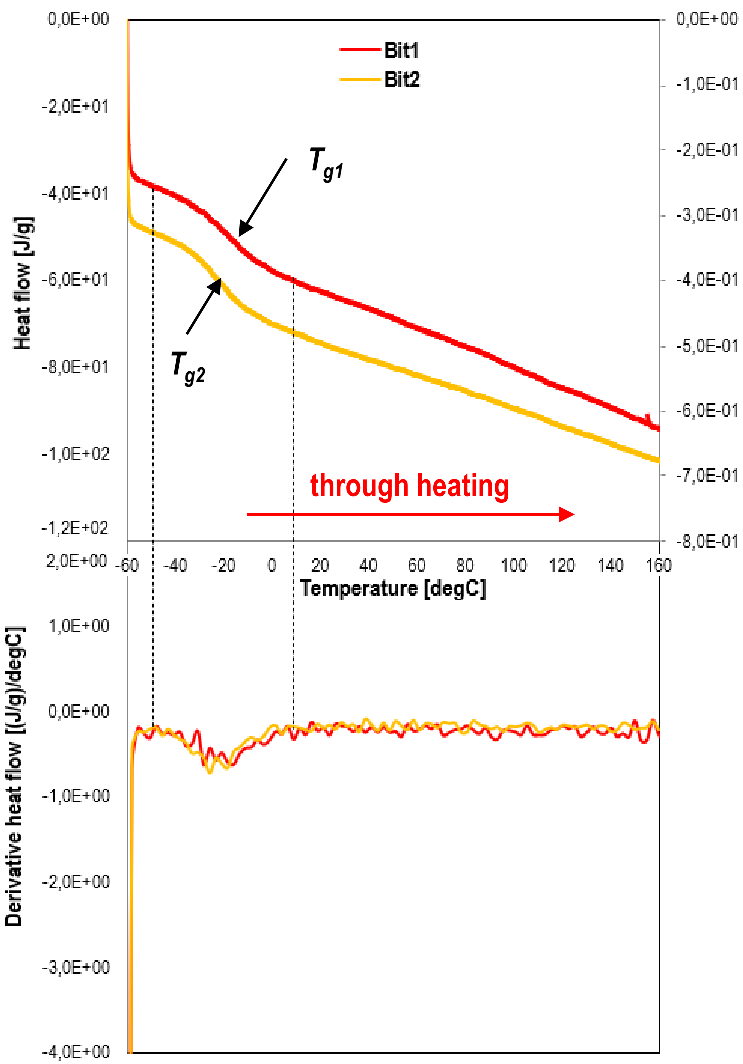
Bit2 – 70/100 penetration graded bituminous binder [PG 64-22]

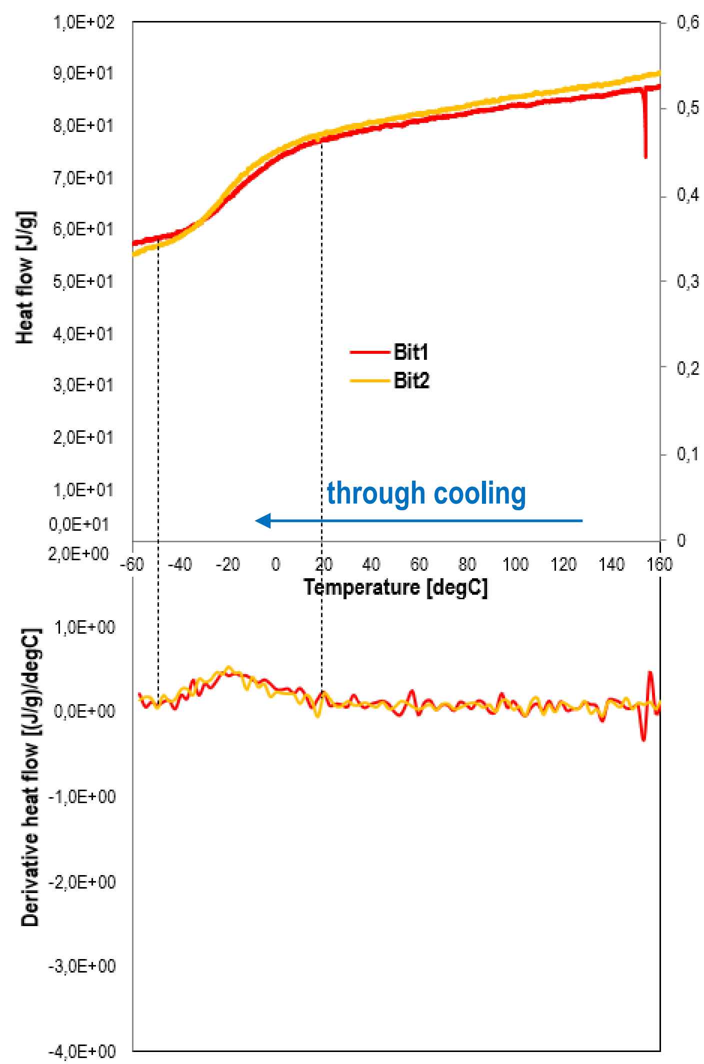
PmB1 – Commercial polymer modified binder (plant-produced) [PG 76-16]

PmB2 – Bit2 modified with 7,5% of SBS (lab-produced) [HiMA, PG 88-28]

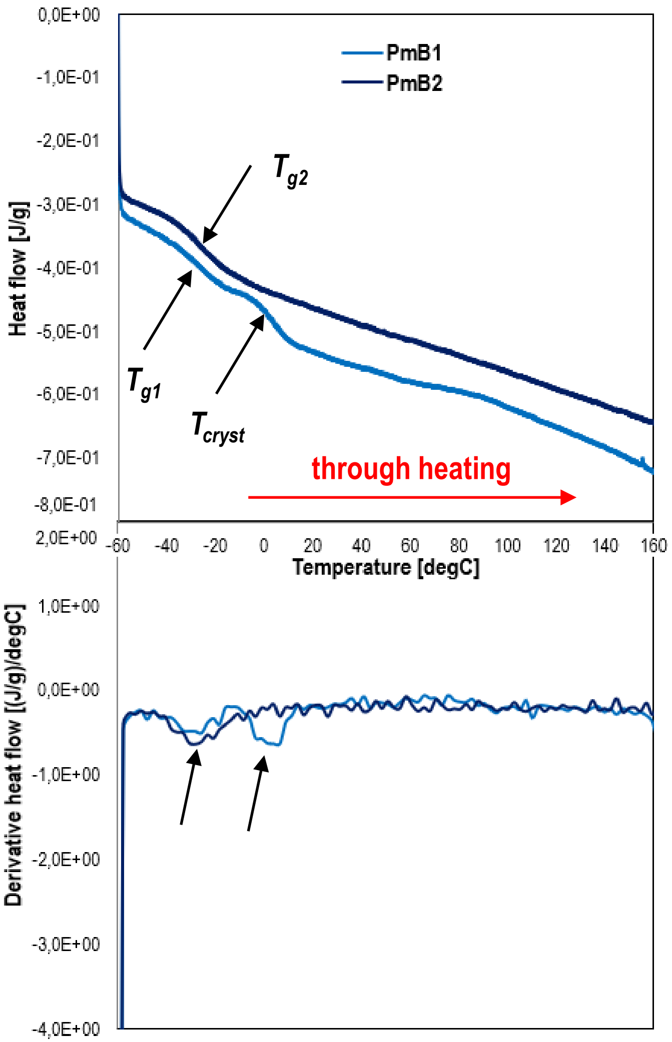
TL-DSC: Heat flow & derivatives

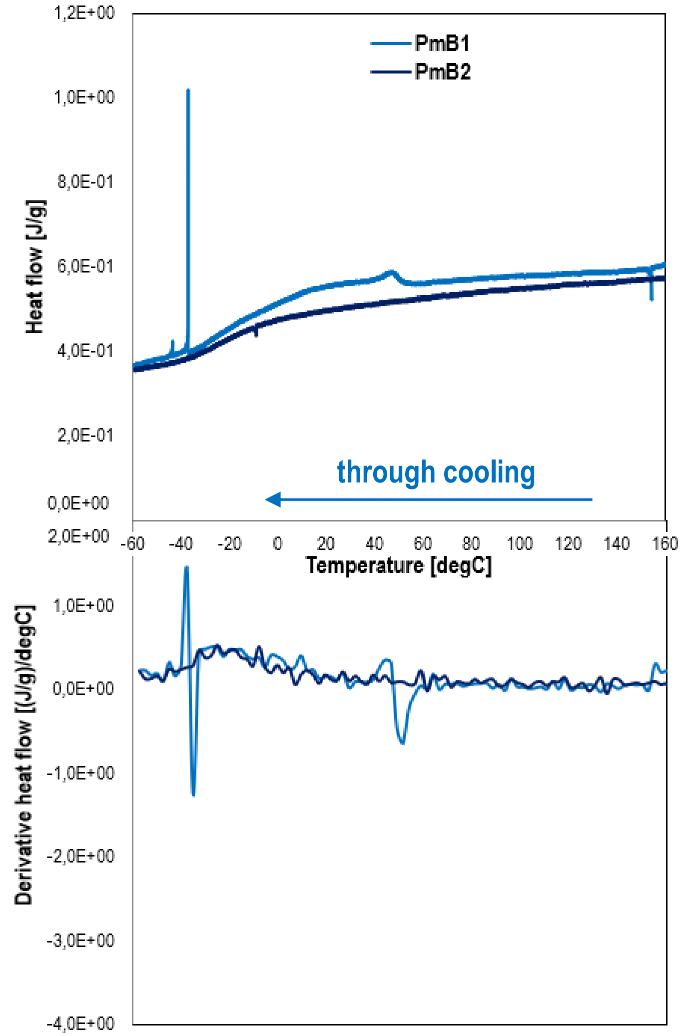
(Bit1 & Bit2, by Lab1)





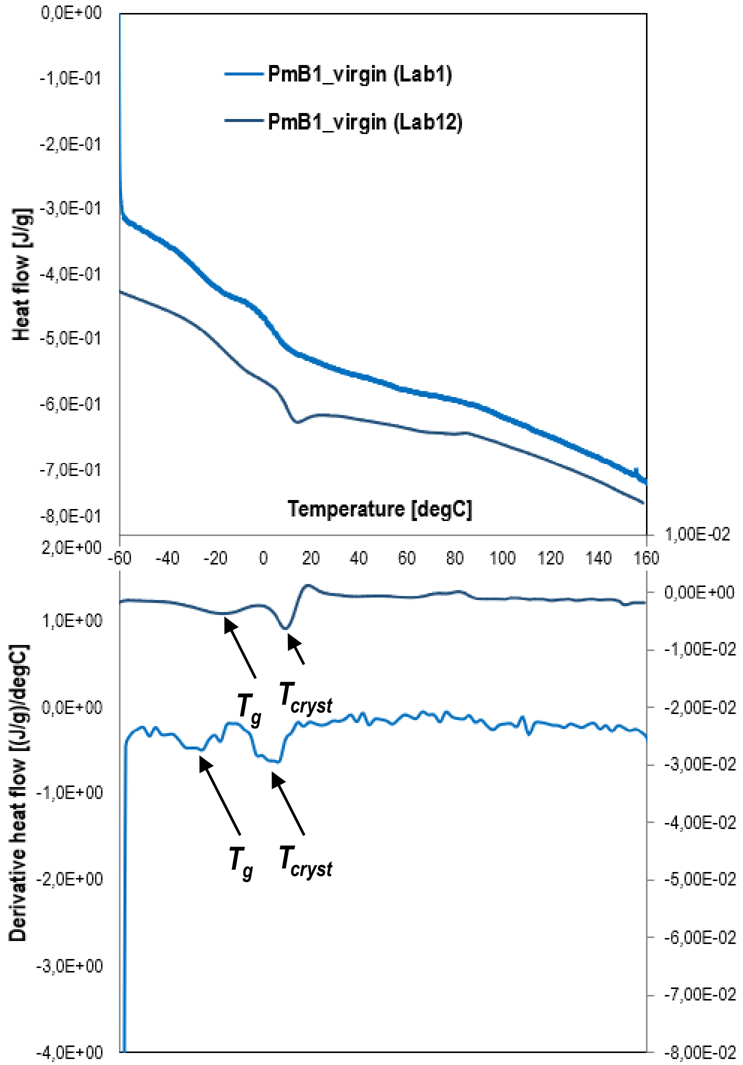
TL-DSC: Heat flow & derivatives
(PmB1 & PmB2, by Lab1)



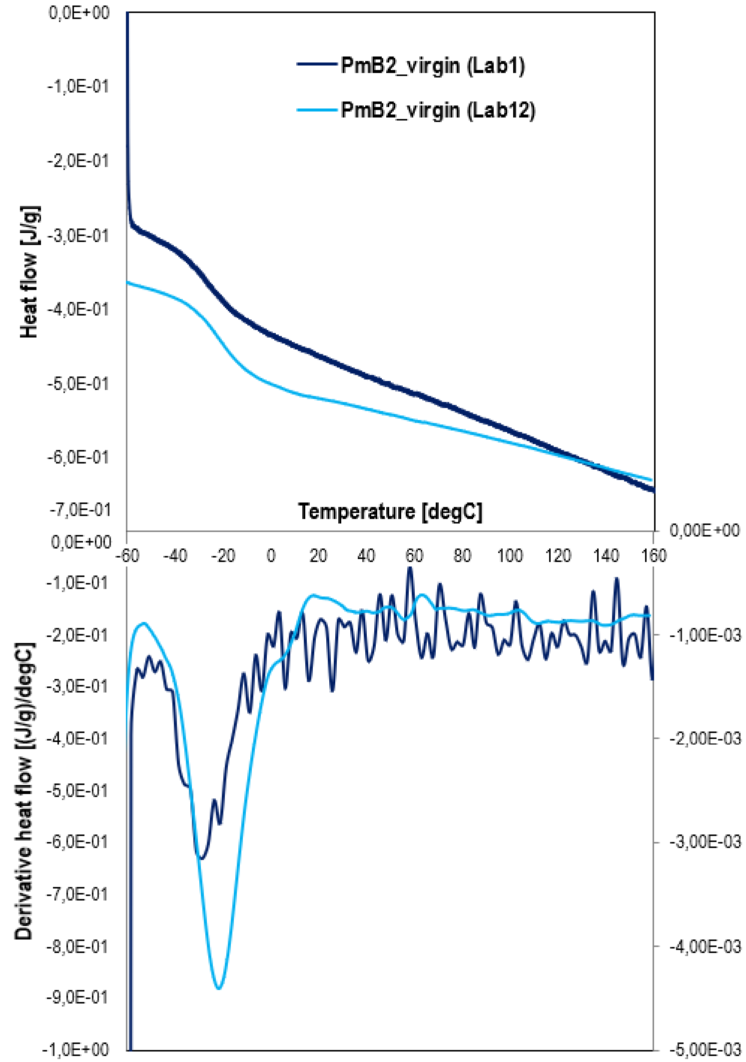


* **Cold crystallization** – the exothermic transition during heating from a solid amorphous to a solid crystalline state.

TL-DSC: With different protocols
(PmB1 & PmB2, through heating)

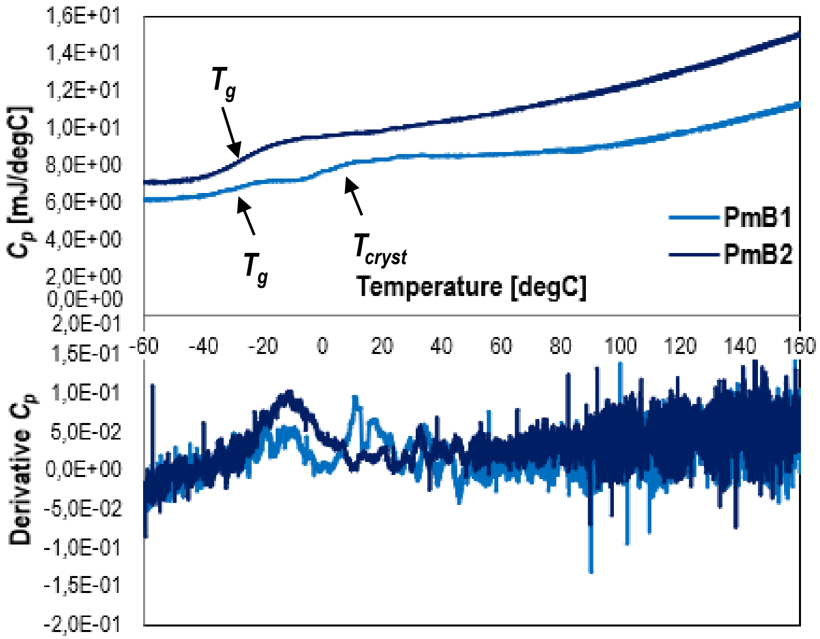


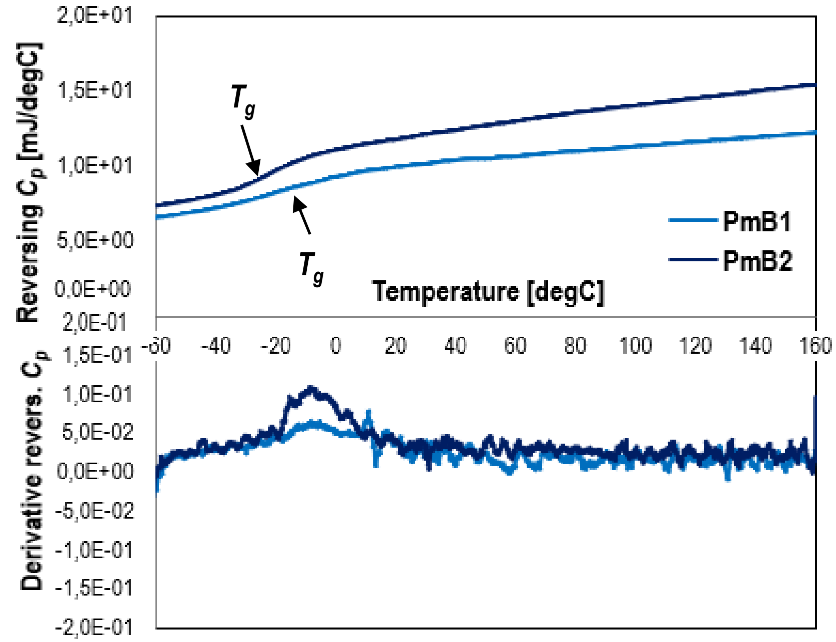
PmB1



PmB2

TM-DSC: Heat capacity & derivatives
(PmB1 & PmB2, through heating)

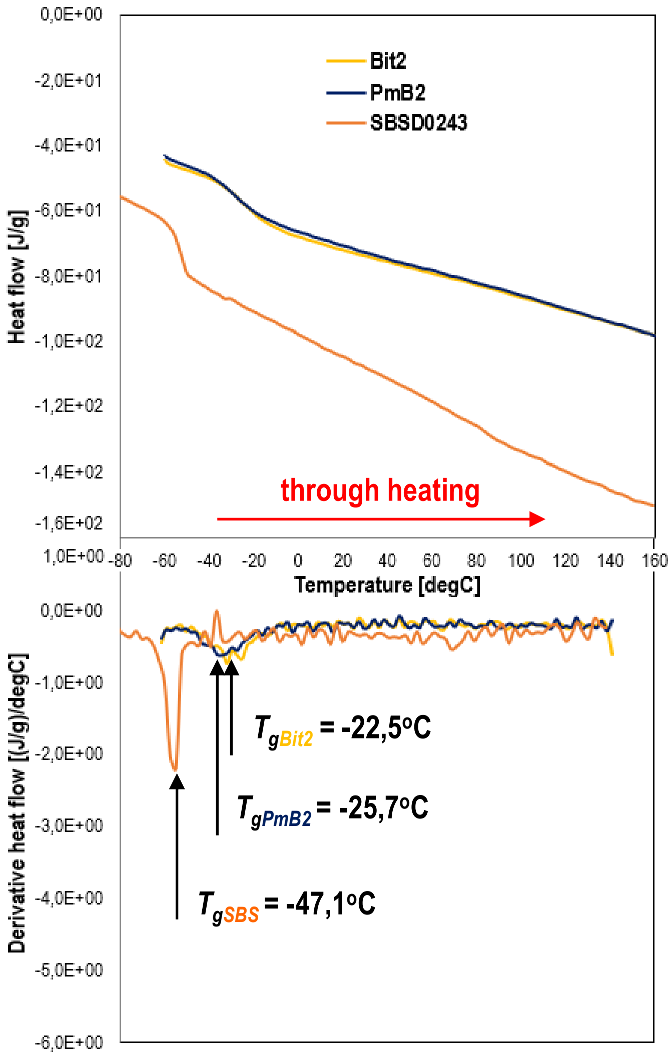


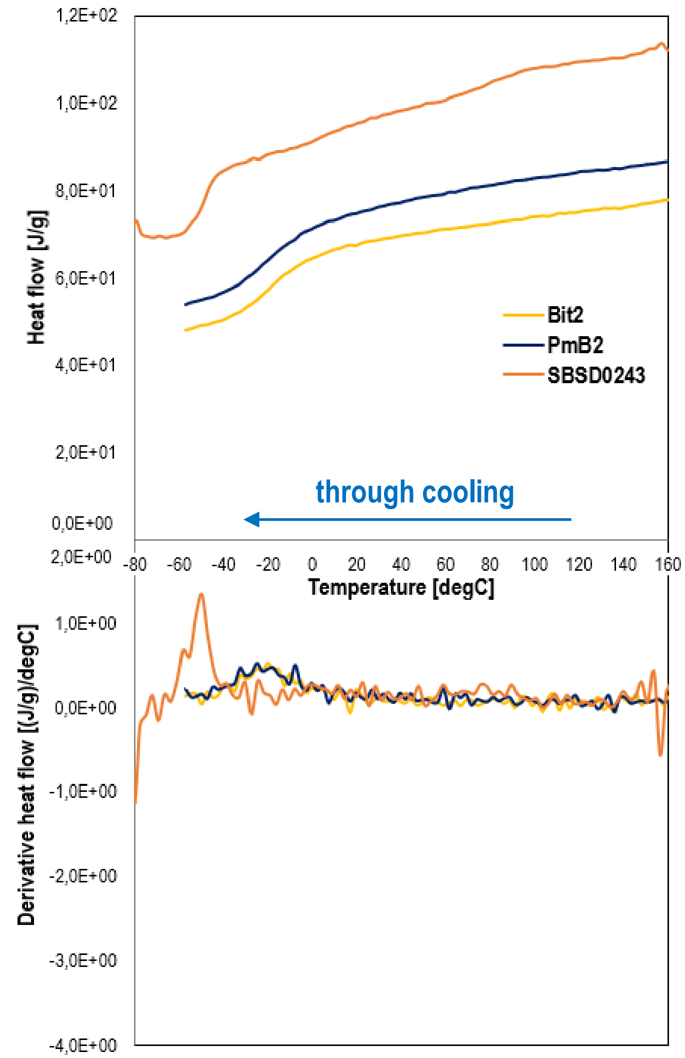


- No cold crystallization in reversing C_p curves.
- The T_g values of binders based on reversing C_p were higher than of total C_p curves.

Impact of SBS

(Bit2, PmB2 & SBS)





* **SBSDO243** - Styrene-butadiene-styrene by KRA | polybutadiene blocks: sharp T_g at ≈ -50degC | polystyrene blocks: broad T_g from 50 to 130degC

Interlaboratory results

T_g values determined based on the 1st derivative of heat flow (TL-DSC) and heat capacity (TM-DSC) through heating measurements

Sample	Glass transition temperature, T_g [°C]			
	Lab1 *1	Lab2 *2	Lab5 *3	Lab12 *4
Bit1	-13,3	-10.5	-16,6	-14,5
Bit2	-22,5	-14.4	-23,3	-18,3
PmB1	-23,2	-16.9	-25,1	-16,8
PmB2	-25,7	-19.2	-25,0	-22,0

*1 TL-DSC: protocol1, *2 TM-DSC: protocol1, *3 TM-DSC: protocol2, *4 TL-DSC: protocol2

Summary of findings so far

- The T_g values were determined by calculating the maximum of the 1st derivative of heat flow and C_p curves during heating.
- In heating TL-DSC,
  - a small reduction in the base-line of heat flow indicates the glass transition in binders,
  - the appearance of a second peak of 1st derivative is a result of cold crystallization. Cold crystallization after the glass transition in PmB1.
- In heating TM-DSC,
  - PmB1 did not show two peaks of 1st derivative of reversing C_p,
  - thus, the TM-DSC allowed the separation of structural relaxation phenomena from the total C_p measurements.
- The polymer modification resulted in the T_g reduction.

Link of DSC with BBR and DSR 4-mm results | Aging studies

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Thank you !