Study of phase behaviour of epoxy asphalt binders with differential scanning calorimetry [PPT]

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Study of phase behaviour of epoxy asphalt binders with differential scanning calorimetry

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Abstract: The glass transition parameters are used to study the miscibility, or lack of it, in polymer modified asphalt binders. In this study, a quantitative assessment of the contribution of thermodynamics of mixing to glass transition was conducted in a differential scanning calorimetry for four asphalt binders modified with an elastomeric epoxy system. Especially, the values of heat capacity (C_p) and subsequently the glass transition temperature (T_g) of all binders were determined to quantify the miscibility based on the entropic changes. Emphasis was also given on examining the enthalpy of mixing as a function of the composition of epoxy asphalt binders during curing to ensure that these binders were completely crosslinked for further analyses. In all cases, the positive deviations of $T_{g,mix}$ obtained from the ideal mixing rule, or $\Delta T_{g,mix}$, led to negative values of the entropy of mixing (ΔS_{mix}^{c}), dictating the presence of internal repulsive forces between the asphalt and epoxy components. The soft in properties and sol type base binders are also associated with epoxy asphalt binders of low $\Delta T_{g,mix}$ values. Overall, the incorporation of the epoxy system in asphalt binders increases the T_g and decreases the amount of ΔS_{mix}^{c}, and such performance imposes the formation of phase-separated binders.

Study of the phase behavior of epoxy asphalt binders using differential scanning calorimetry

2022 Petersen Asphalt Research Conference

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Outline

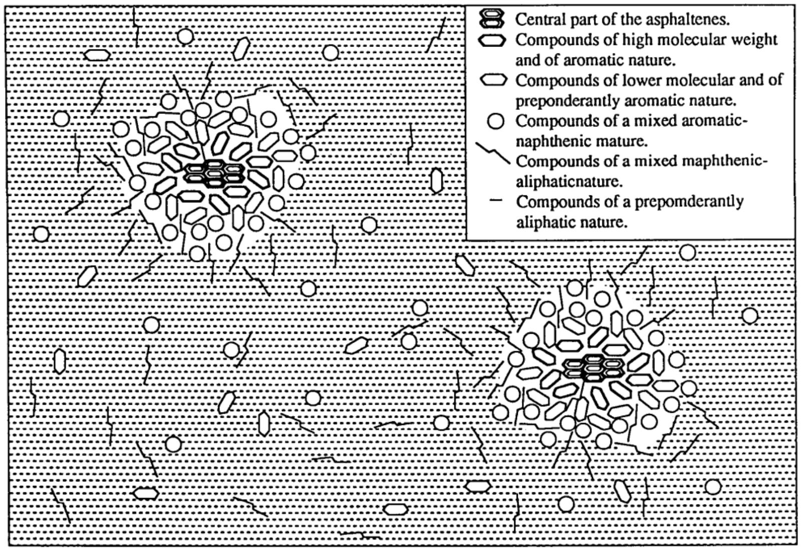
- **Motivation & Scope**
- **Binders & Set-up**
- **Results**
- **Future Research**

Epoxy in Asphalt Binders

previous studies

	AAD-2	AAG-2
PG grade	PG 52-34	PG 58-16
Continuous PG grade	PG 56,52-35,34	PG 61,22-18,83
Viscosity at 140°F [poise]	600	1056
Softening point [°F]	117	111
Penetration at 77°F [0.1-mm]	195	76
Component analysis		
Asphaltene, n-heptane [%]	21.3	5.0
Asphaltene, iso-octane [%]	3.1	2.8
Polar aromatics [%]	40.1	51.0
Naphthene aromatics [%]	26.7	35.3
Saturates [%]	10.0	6.6

SHRP 645A, 1993.



SHRP-A/WP-90-008, 1990.

AAD-2 (high-asphaltene content) → Gel-type binder → High curing rate with epoxy

AAG-2 (low-asphaltene content) → Sol-type binder → Low curing rate with epoxy

Mensching, D., et al. 2020, Epoxy modified asphalt: Dilution and curing exploration. TRB, Washington, DC.
Elwardany, M.D., et al. 2021. Base-binder-dependent reactivity in epoxy-modified asphalt. PARC, Laramie, WY.

Scope

- ❑ Understand the effect of epoxy systems on the glass transition of asphalt binders,
- ❑ Provide insights into the phase behavior of epoxy asphalt binders based on glass transition measurements,
- ❑ Guide the selection of binders for epoxy modification and potentially other reactive polymers.

Materials

binders

Asphalt

***US source*: PG 64-22 [VA], PG 67-22 [FLO]**
***European source*: 70/100 pen & 160-220 pen**

Epoxy

Commercial epoxy-asphalt binder (ChemCo Systems)

New binders

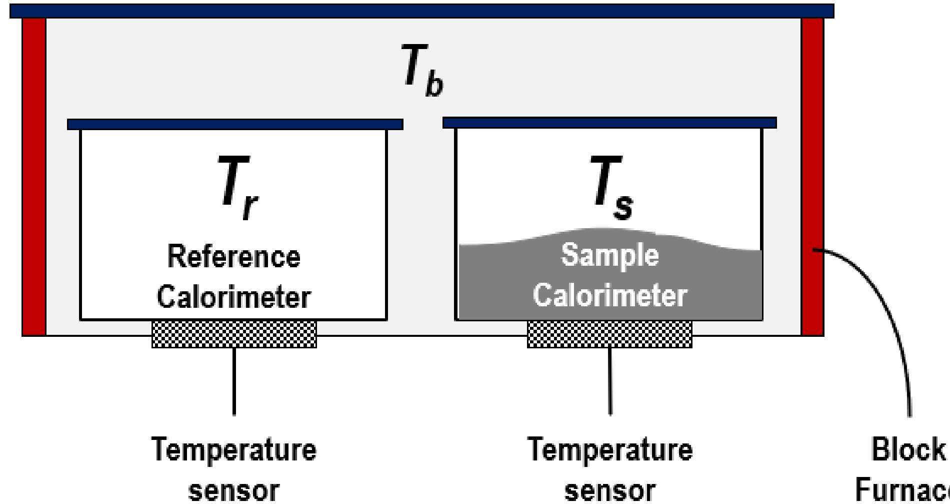
Epoxy:Asphalt = 0:100, 20:80, 50:50, 100:0 [% wt ratio] **

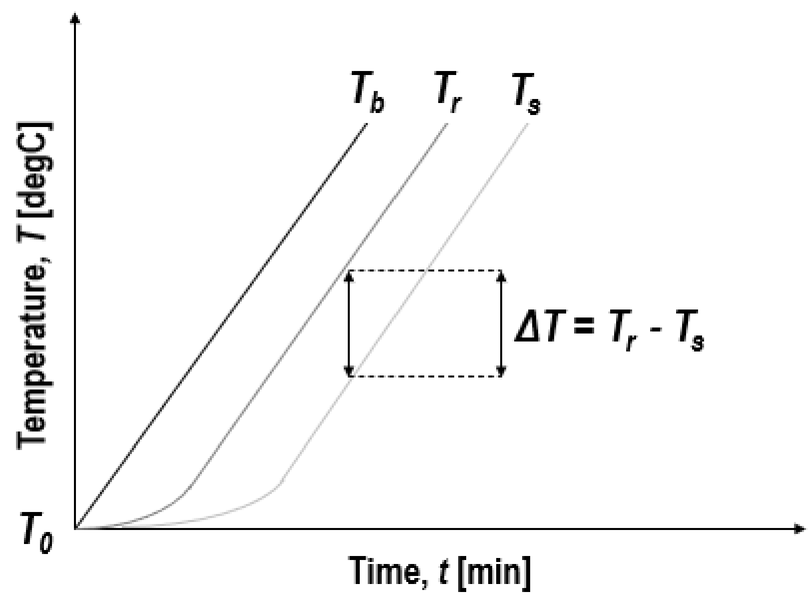
** EA0, EA20, EA50 and EA100

Differential Scanning Calorimetry (DSC)

set-up

DSC, PerkinElmer



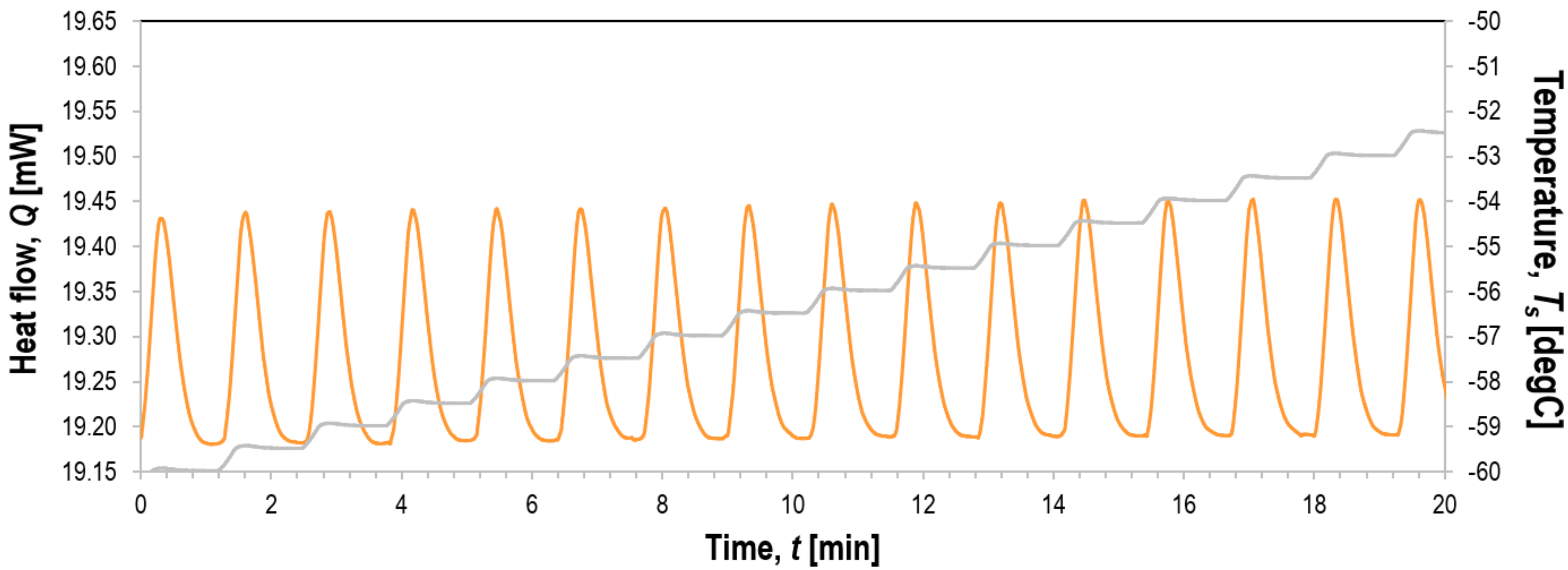


Modulated Differential Scanning Calorimetry (MDSC)

temperature modulation

1	Isothermal | -60 degC	for 5 min
2	Modulation | 5 degC/min	to 300 degC
3	Isothermal | 300 degC	for 5 min
4	Modulation | 5 degC/min	to -60 degC

Sample mass : between 5 and 10 mg



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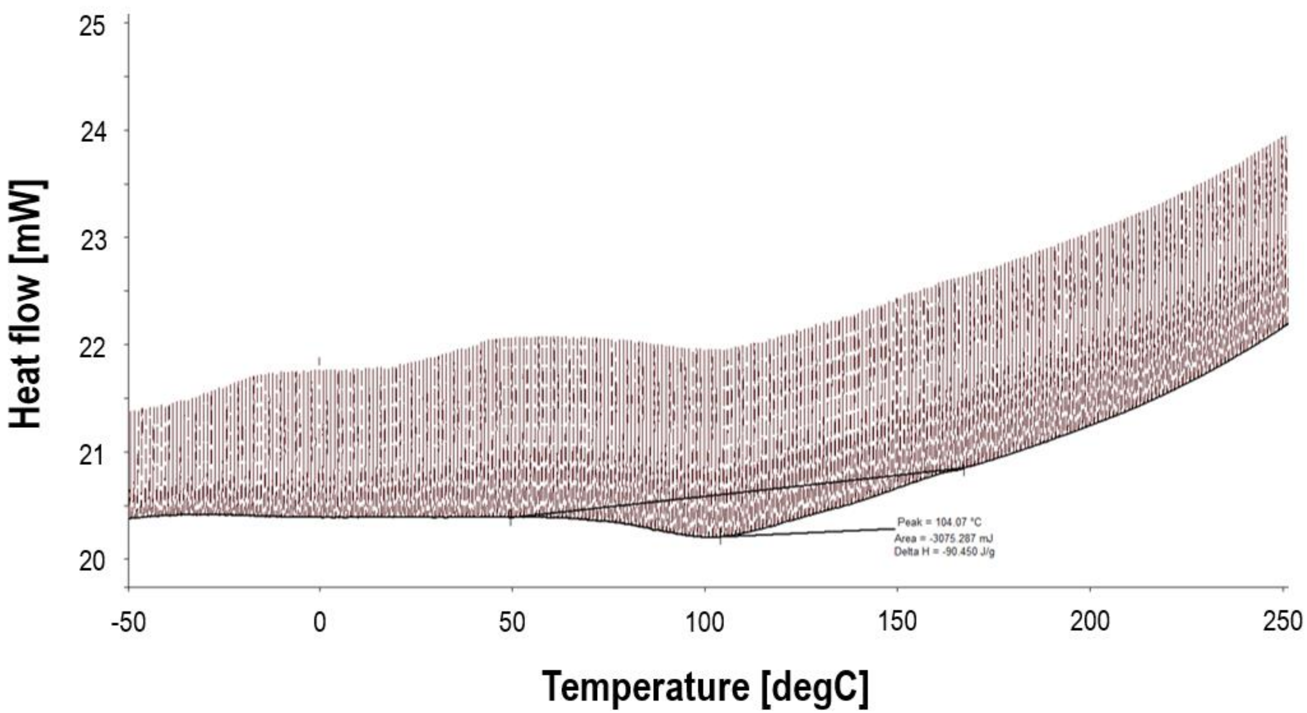
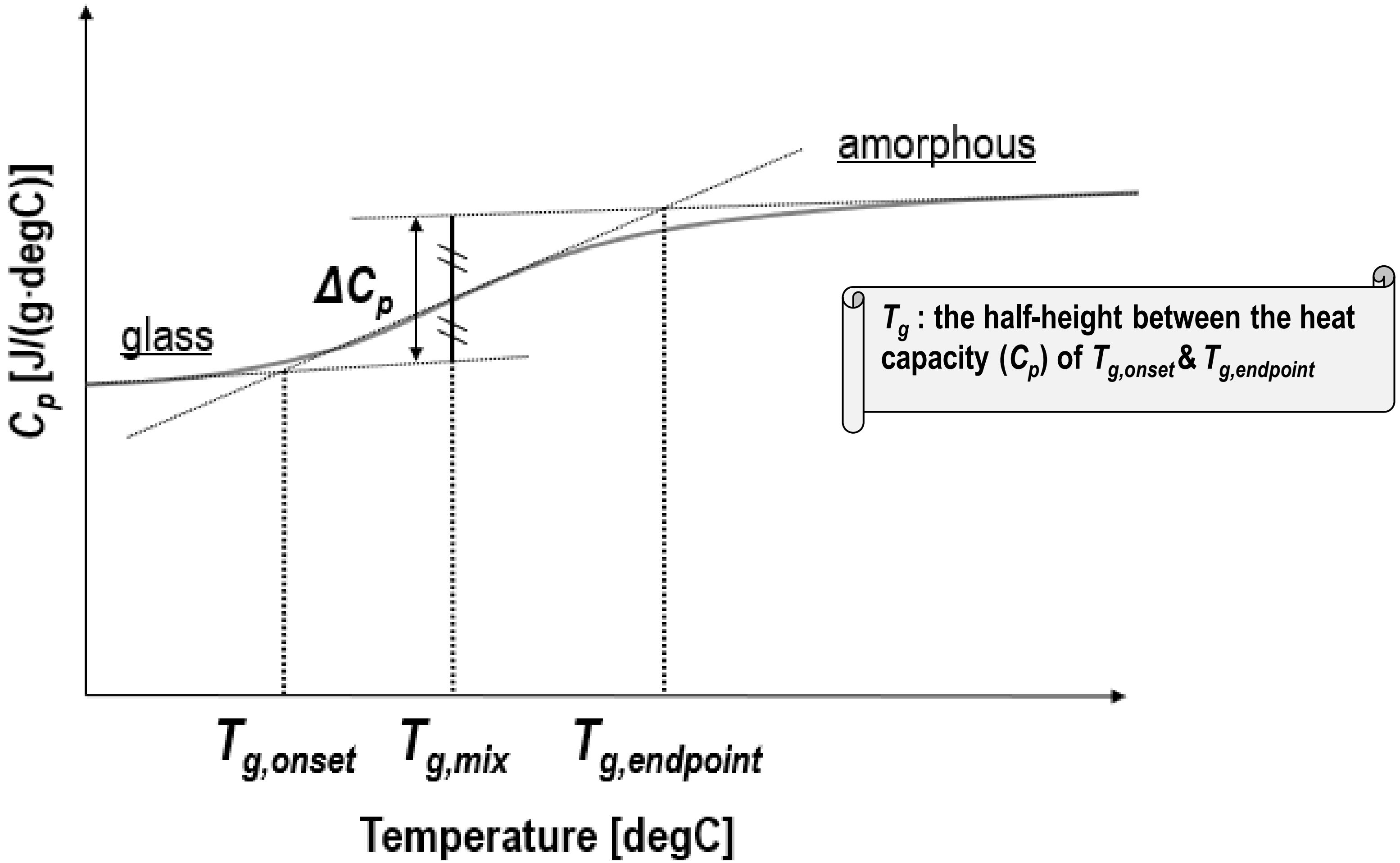


Modulated Differential Scanning Calorimetry (MDSC)

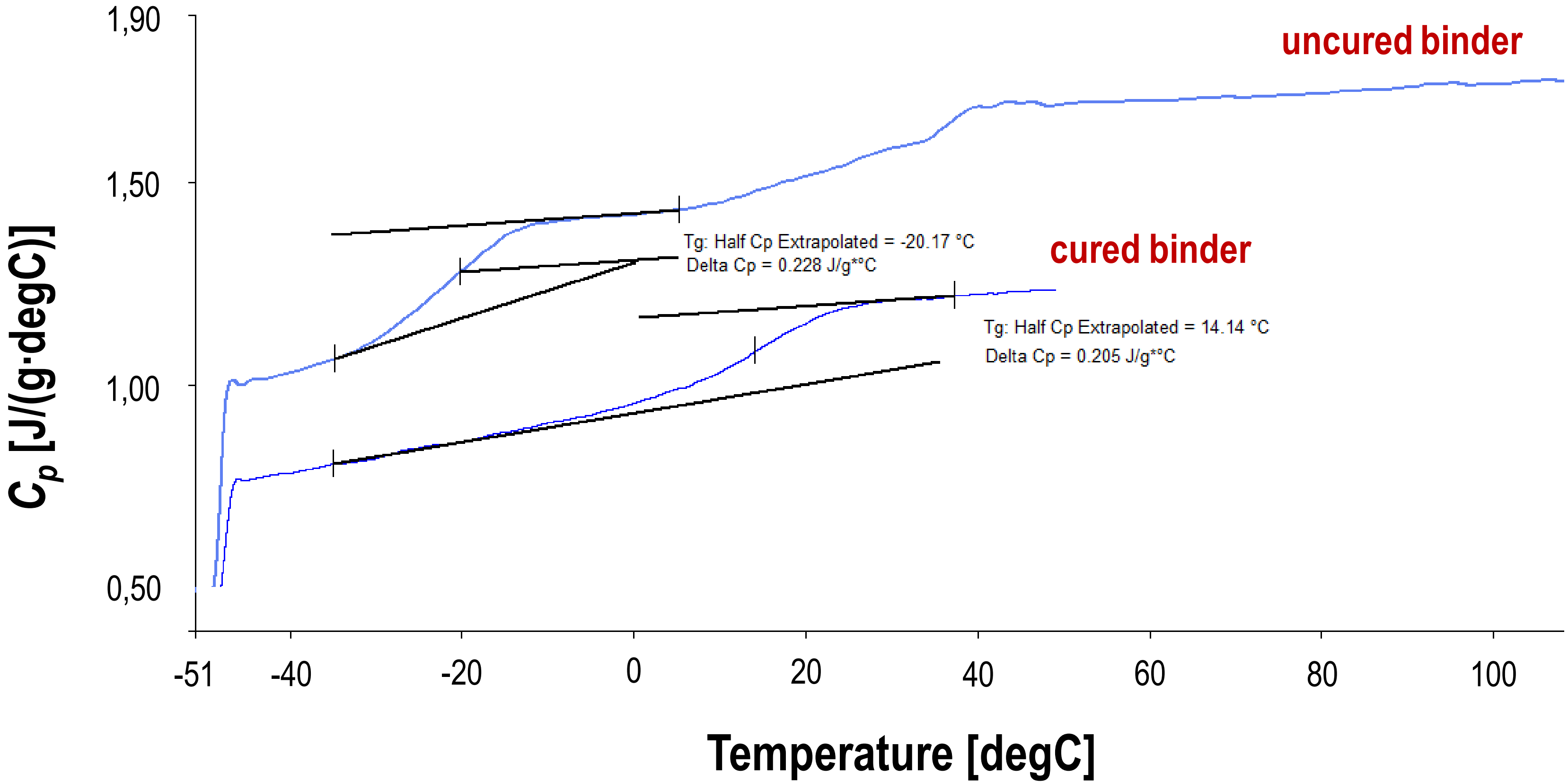
to measure the glass transition of binders



- Binders behave as glass below the glass transition temperature (T_g), while above the T_g they behave as amorphous.
- The glass transition can assist on understanding the thermal cracking of binders.

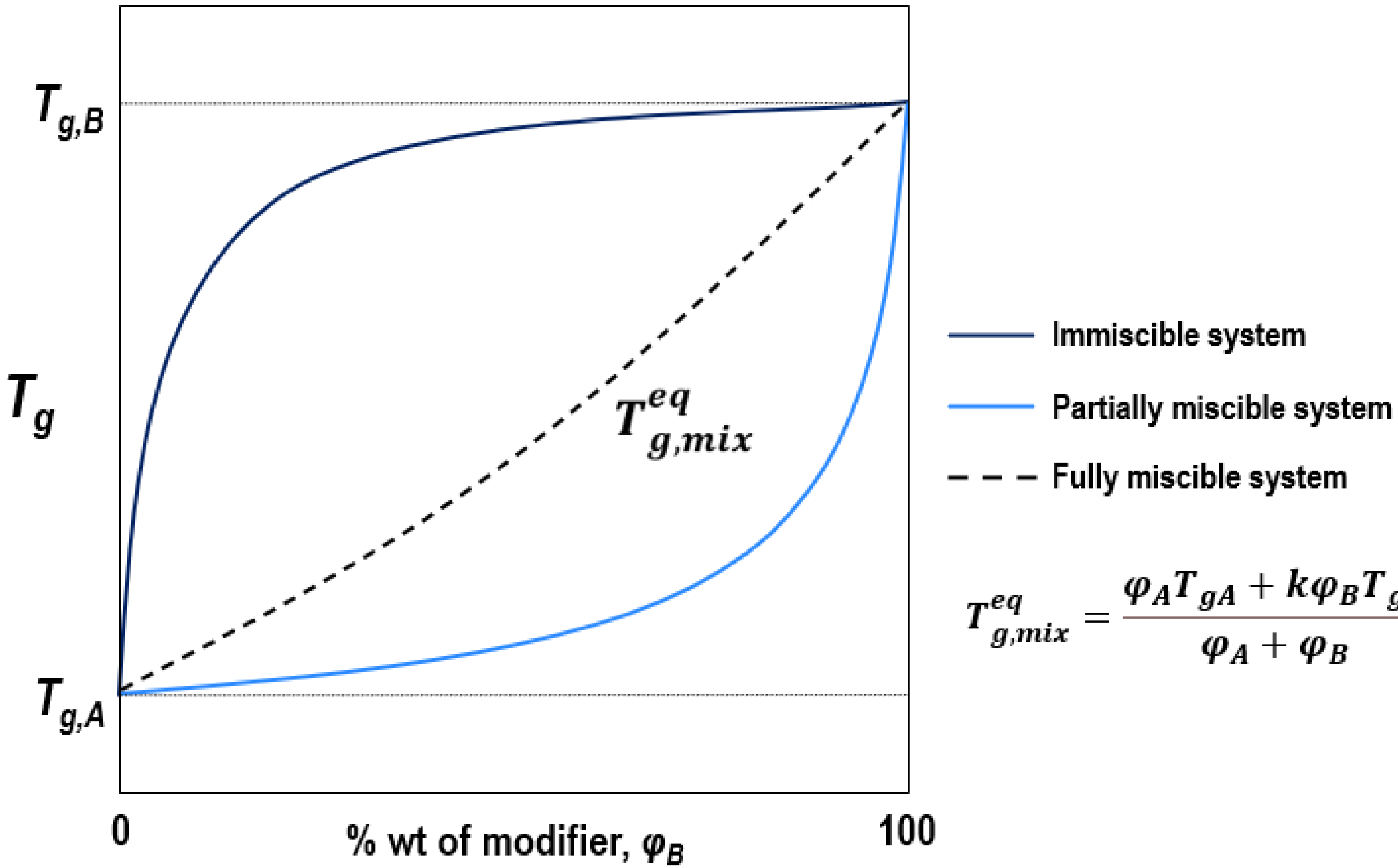
Heat Capacity vs Temperature

of uncured and fully cured epoxy-asphalt binder



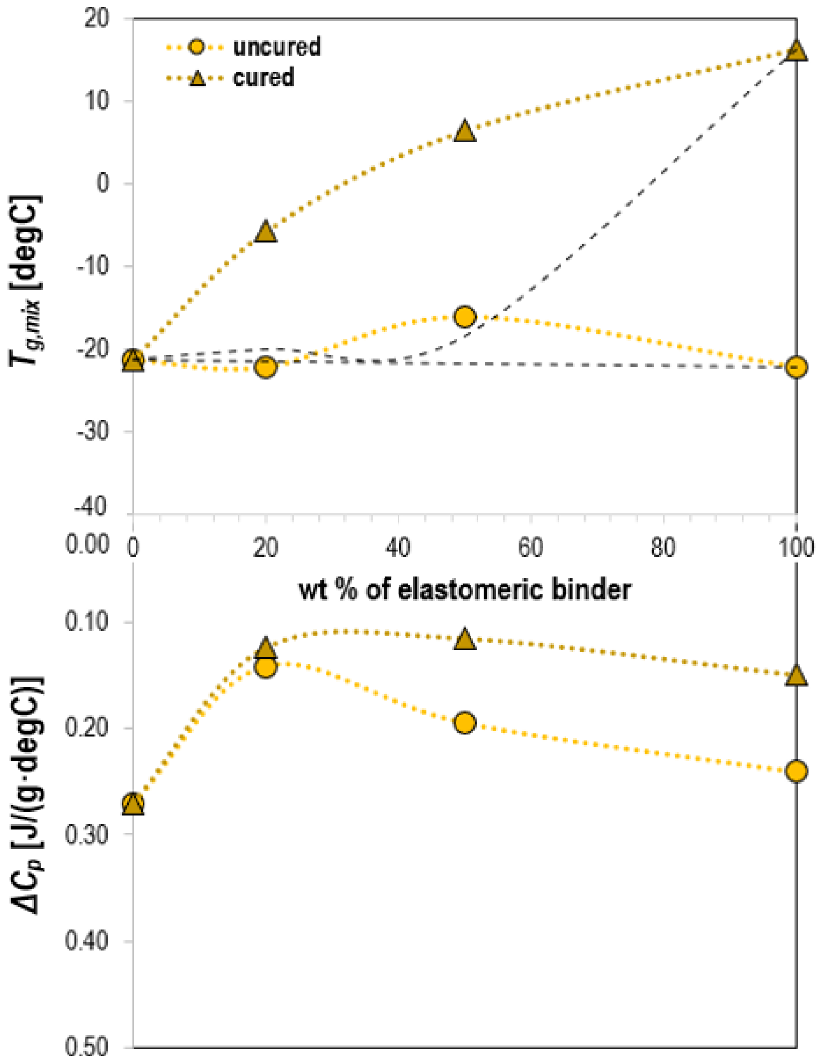
Phase Behavior Analyses with DSC

composition dependence of glass transition in a binary binder

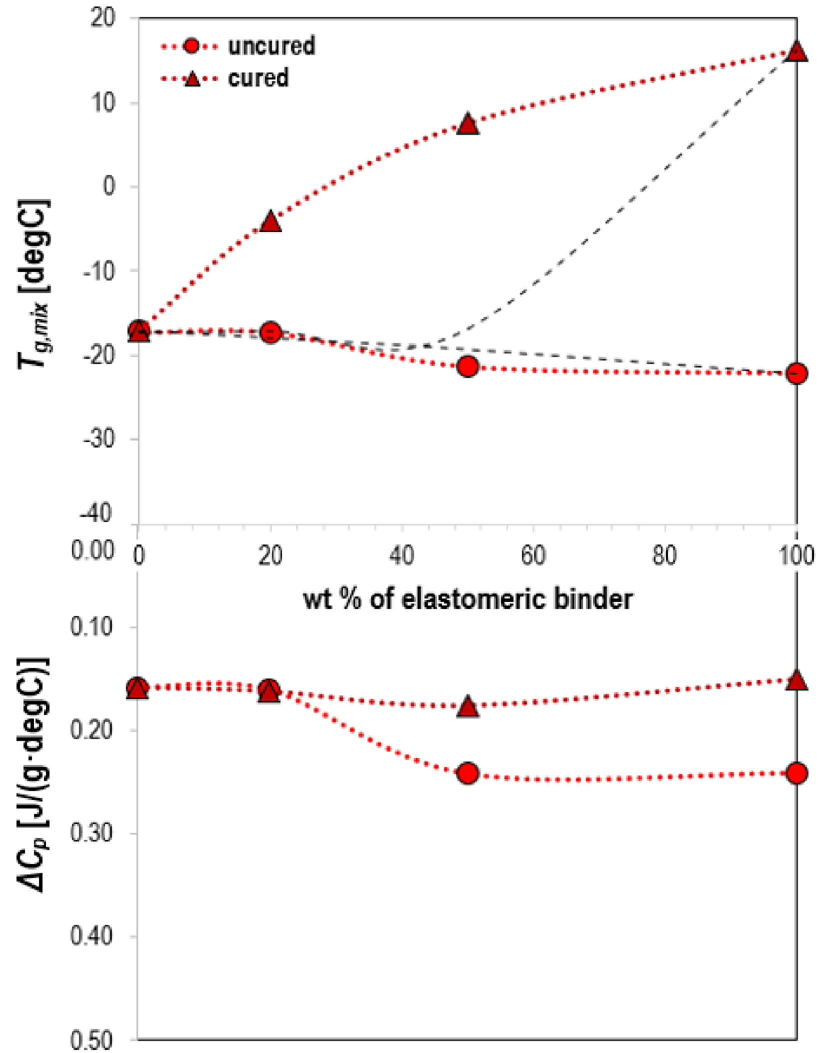


$$T^{eq}_{g,mix} = \frac{\varphi_A T_{gA} + k\varphi_B T_{gB}}{\varphi_A + \varphi_B}$$

Composition Dependence of T_g and ΔC_p

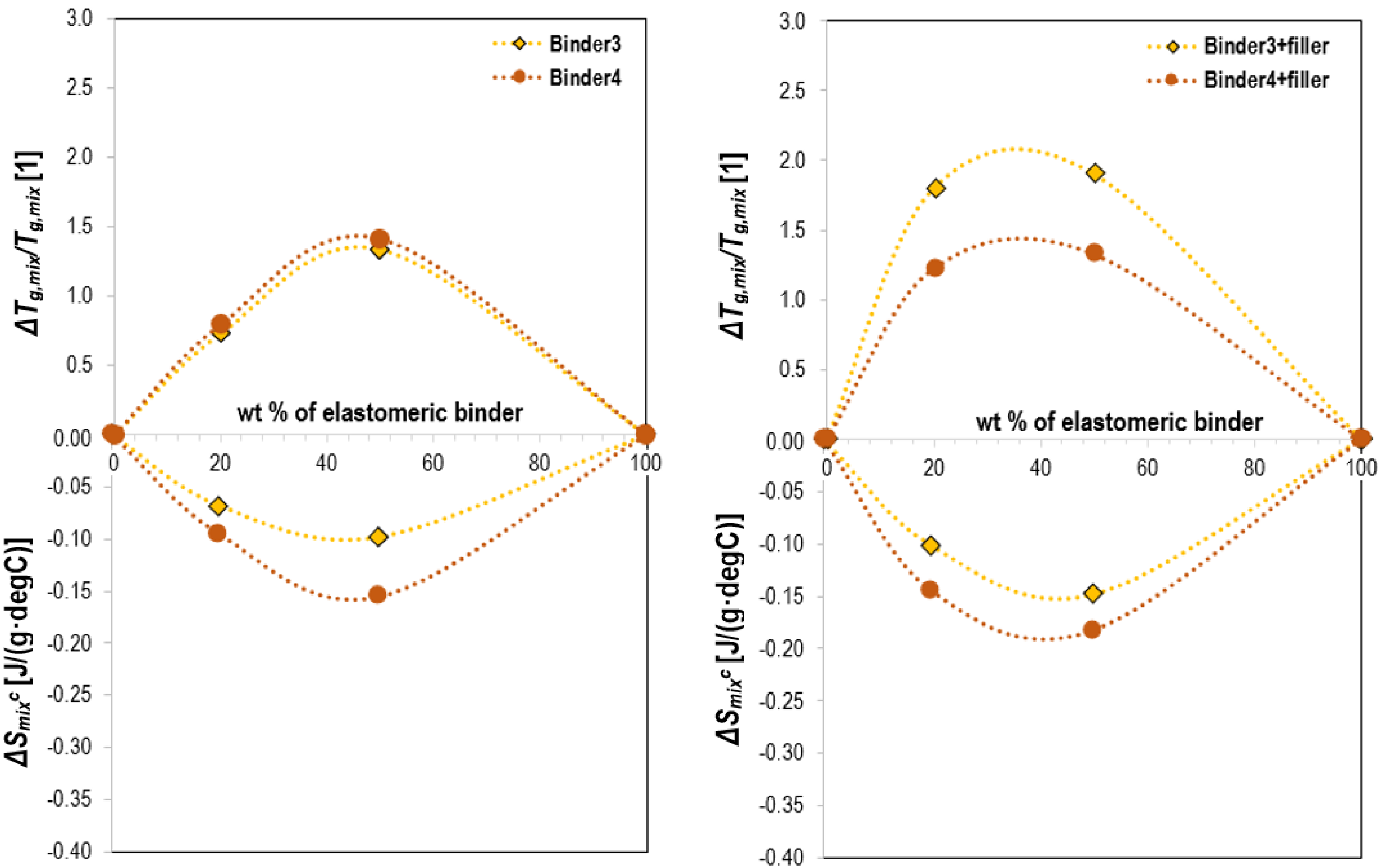


PG 67-22 [FLO], or Binder3



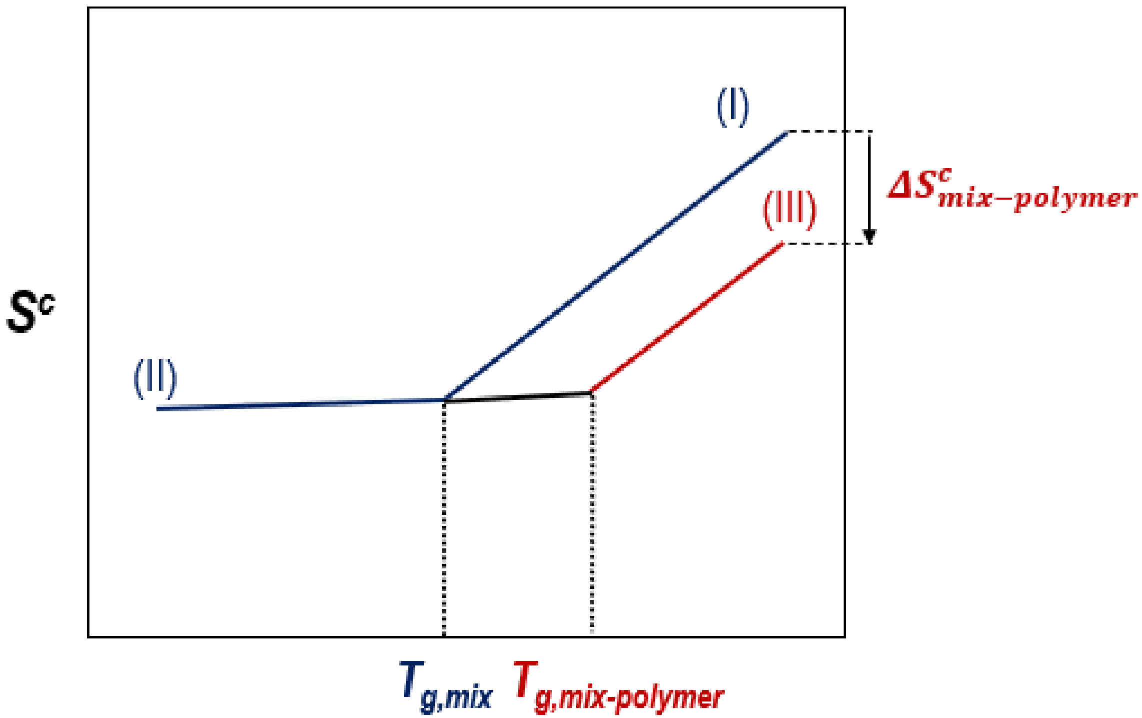
PG 64-22 [VA], or Binder4

Composition Dependence of $\Delta T_g/T_g$ and ΔS_{mix}



Binders **Binders with filler**

Epoxy in Asphalt Binders



(I) neat asphalt binder at amorphous state

(II) neat asphalt binder at glass state

(III) epoxy asphalt binder at amorphous state

Summary

the main findings are:

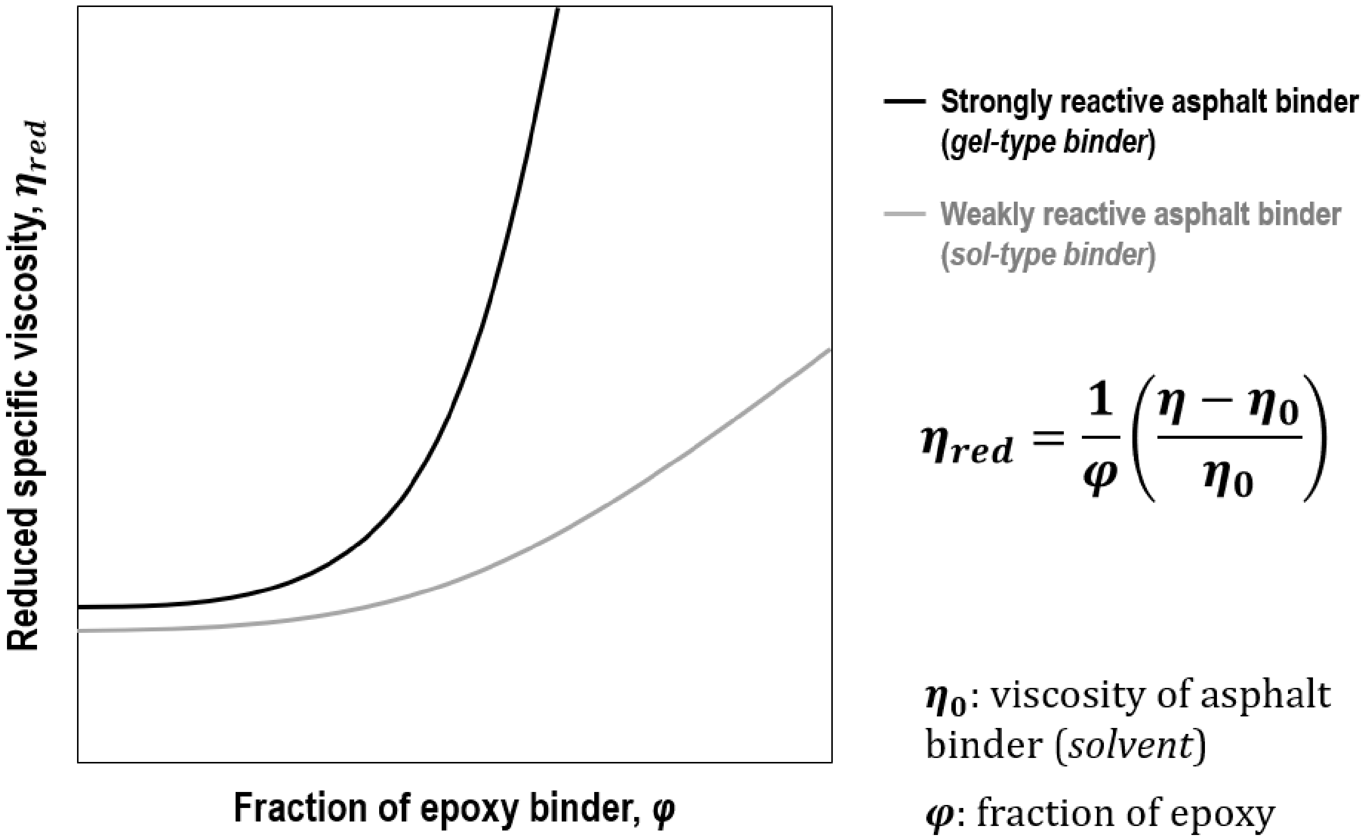
- The T_g increased with the increase of polymer in base asphalts,
- Similar composition dependence of T_g was observed in cured binders but with variations in T_gs based on the base asphalts,
- The positive deviations of T_gs from the ideal mixing, or $\Delta T_{g,mix}$, led to negative ΔS_{mix}^{c} values, dictating the presence of internal repulsive forces between polymer and base asphalt binder,
- The soft in properties or sol type base asphalts are associated with low and positive $\Delta T_{g,mix}$ values, and to a less phase-separated epoxy asphalt binders.

in the future ...

Future: Phase Behavior Analyses

new methods can be developed using:

- infrared spectrometers (e.g., FTIR)
- viscometers (e.g., Brookfield)



$$\eta_{red} = \frac{1}{\varphi}\left(\frac{\eta - \eta_0}{\eta_0}\right)$$

η_0: viscosity of asphalt binder (*solvent*)

φ: fraction of epoxy binder (*solute*)

Future: Embrittlement Analyses

to link glass transition with fracture mechanics parameters

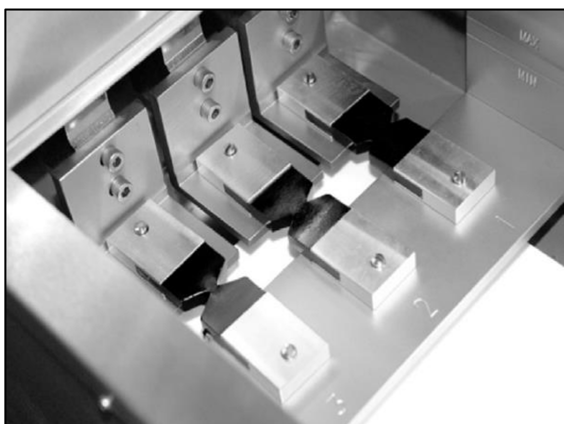
Glass transition

- Glass transition temperature
- Specific heat capacity

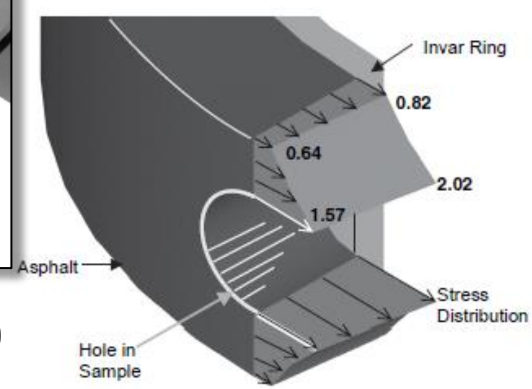
↔

Fracture mechanics

- Parameters from DENT, or
- Parameters from ABCD
- …



Andriescu, A., & S.A.M. Hesp. 2009
https://doi.org/10.1080/10298430802169440



Highway IDEA Project 99, 2007

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Thank you