Glass Transition Distribution in Miscible Polymer Blends: from Calorimetry to Rheology

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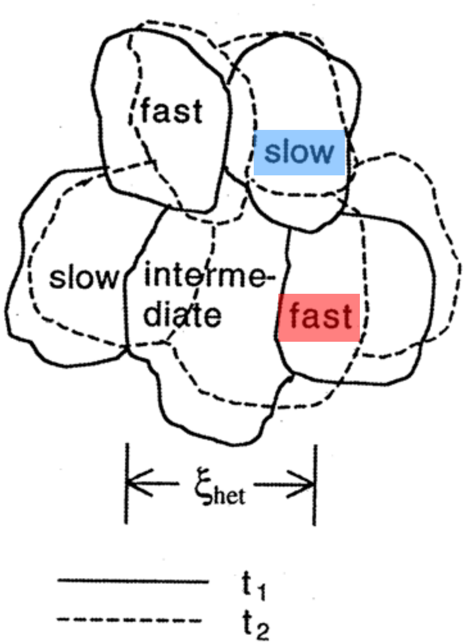
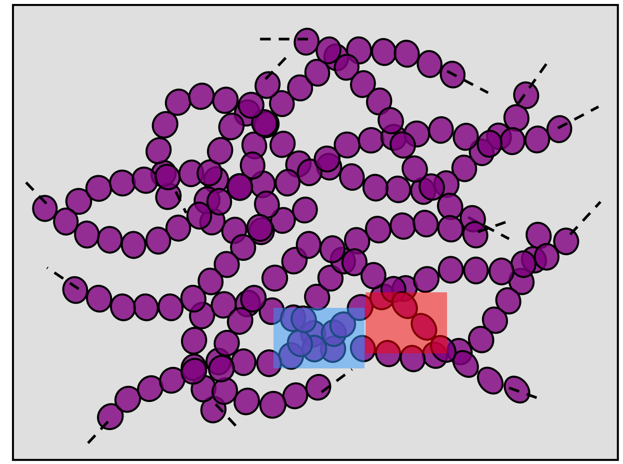
Classic picture of glasses: “dynamic heterogeneity”

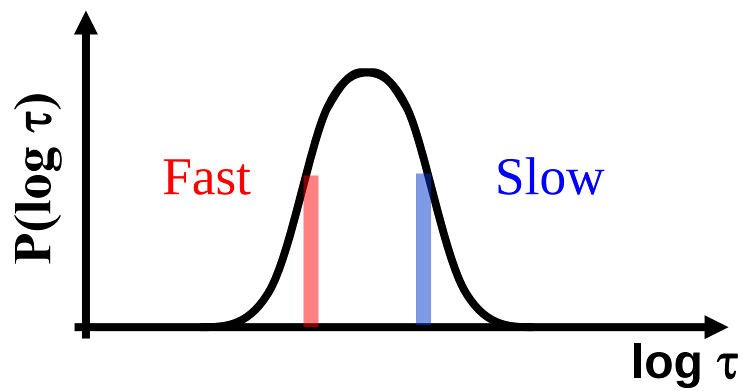
[Ediger, Review, 2000]



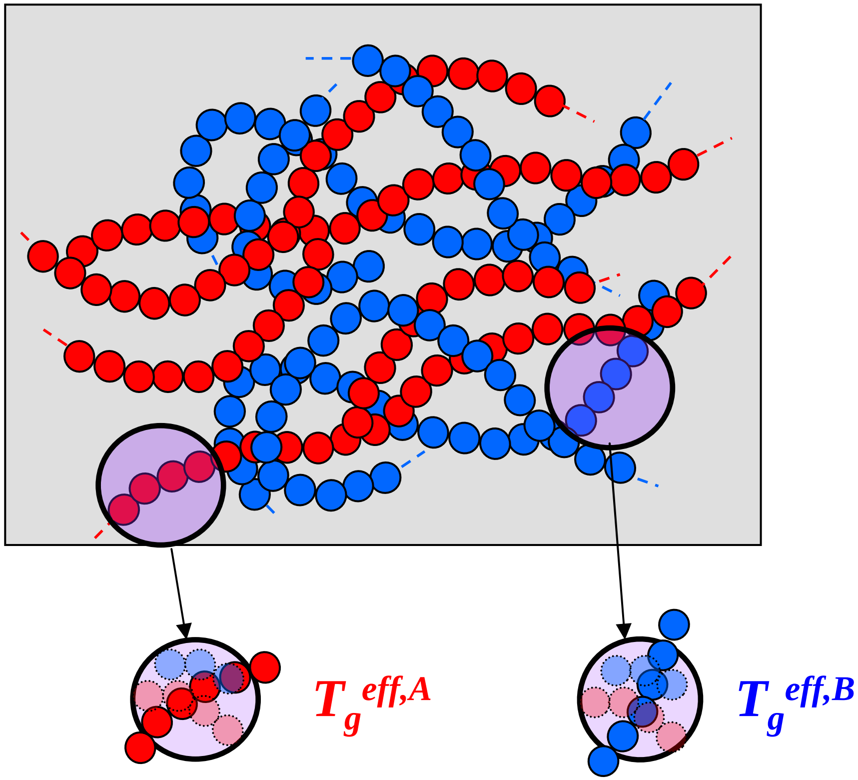
« Schematic illustration of regions of spatially heterogeneous dynamics near Tg. These regions are on the order of ξ_{het} in dimension (typically a few nanometers) and evolve in time. »



A glassy polymer



Classic picture of miscible polymer blends: dynamic asymmetry



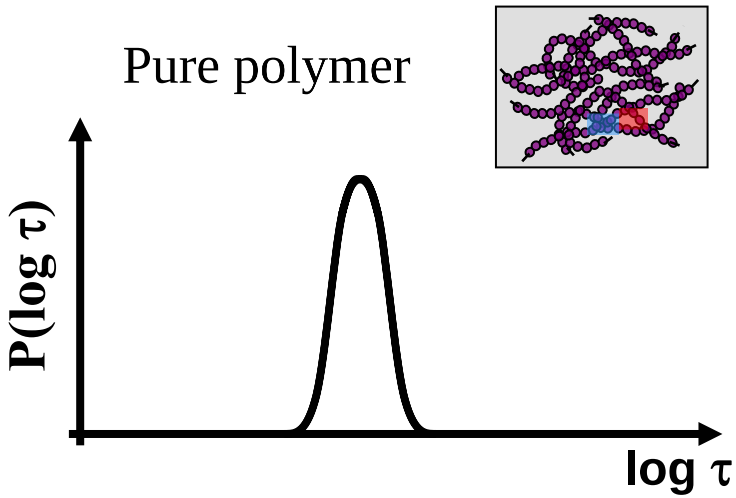
Fast component, low Tg

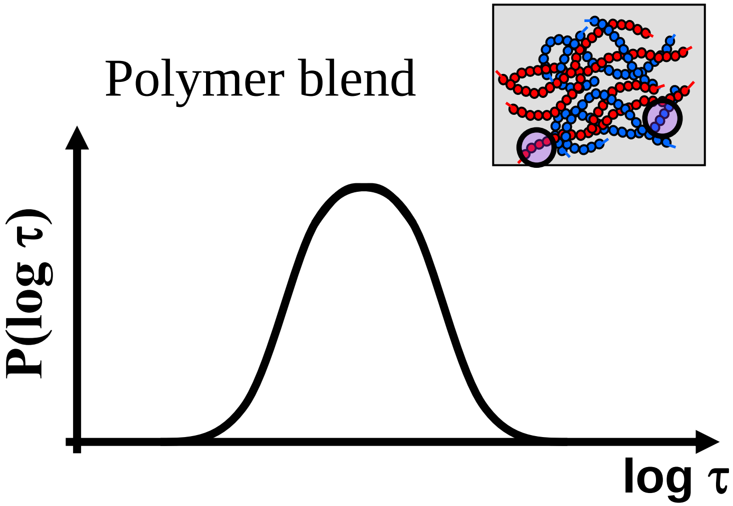
Slow component, high Tg

Great ΔTg ➔ dynamic asymmetry

Self-concentration (Lodge & McLeish, Colby, etc…)

Miscible polymer blends: dynamic asymmetry





➔ Glass Transition Distribution??

- Calorimetry
- Physical aging
- Rheology

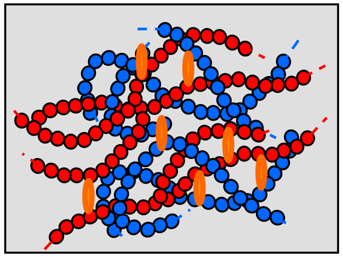
Outline

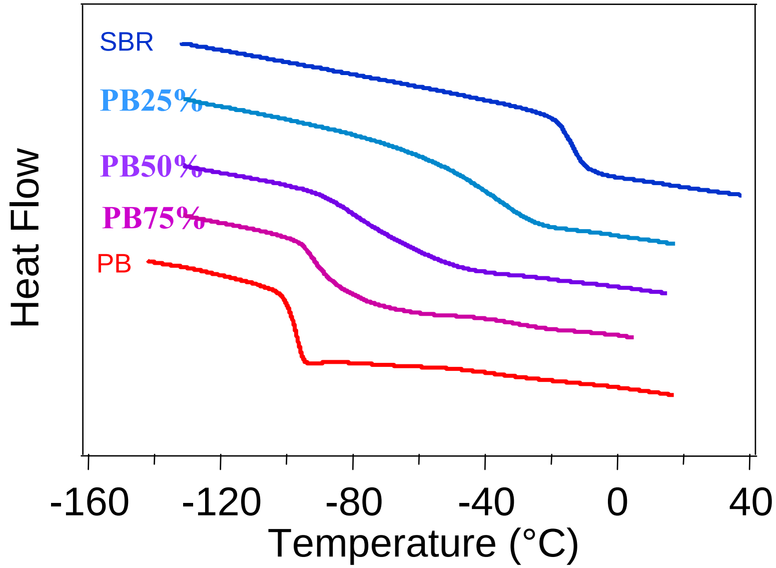
- From calorimetry to *P(Tg)* of blends
- Physical aging of blends
- Rheology prediction
- Conclusion

Our blends PB/SBR

- PB: Polybutadiene, Tg ~ -100°C, l_k~10Å
- SBR: random Styrene-Butadiene copolymer, Tg ~ -15°C, l_k~12Å

All blends are mixed in common solvent and **crosslinked**.





PI/PVE blends

[Lodge & McLeish, 2000]

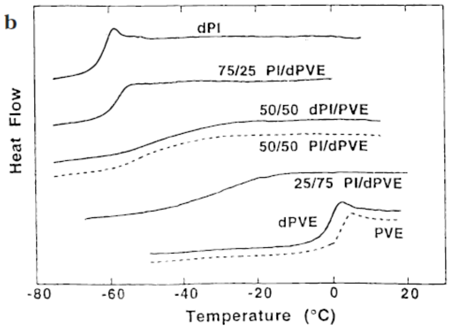
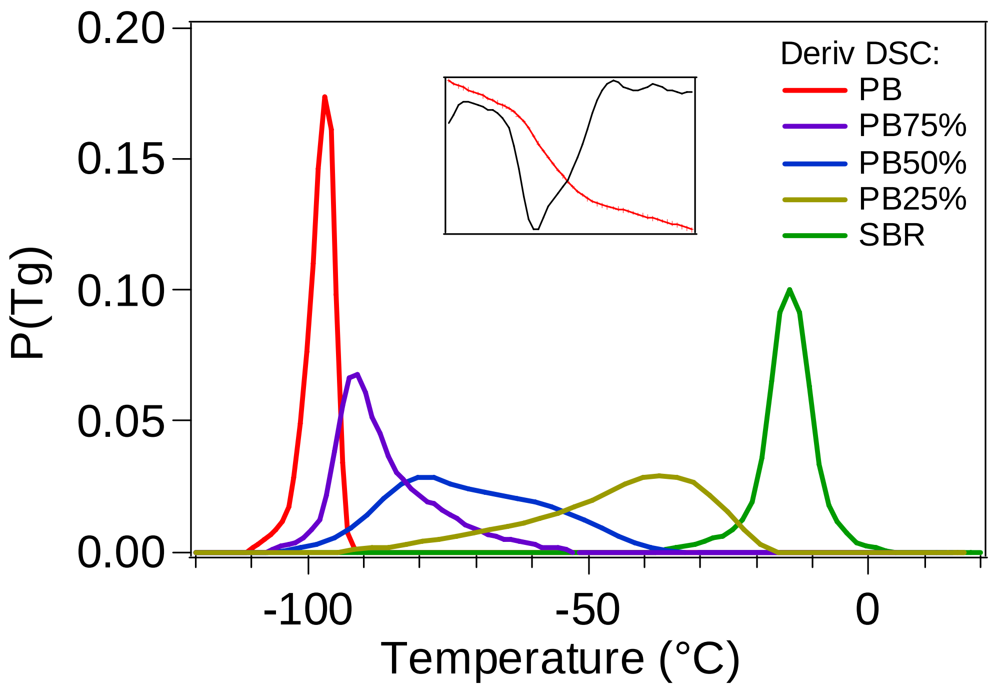


Figure 5. (a) Effective glass transition temperatures and (b) dsc traces for PI/PVME blends; data from Chung et al.[13]

➔ A single and very broadened *Tg* for our blends.

From Calorimetry to *P(Tg)*

$P_{deriv}(Tg)$ ~ Temperature derivative of the heat flow.



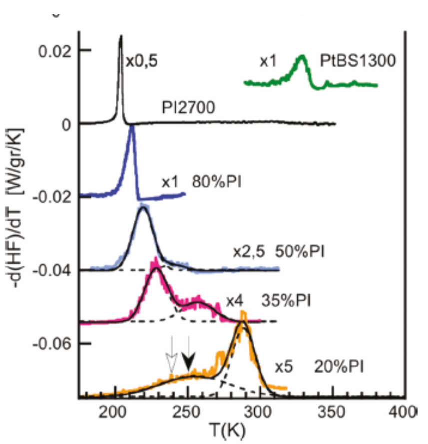


Figure 1. Lower panel: Derivative of the heat flow with respect to T for PI2700 and PtBS1300 homopolymers and their blends at different compositions (color on line). The intensity of the curves was multiplied

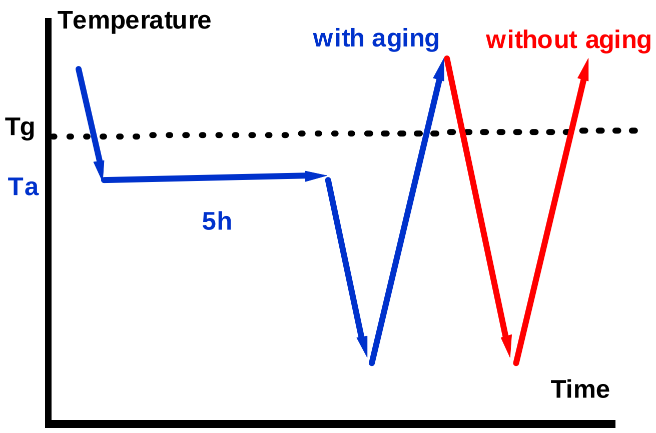
[Arrese-Igor, Alegria, and Colmenero, 2010]

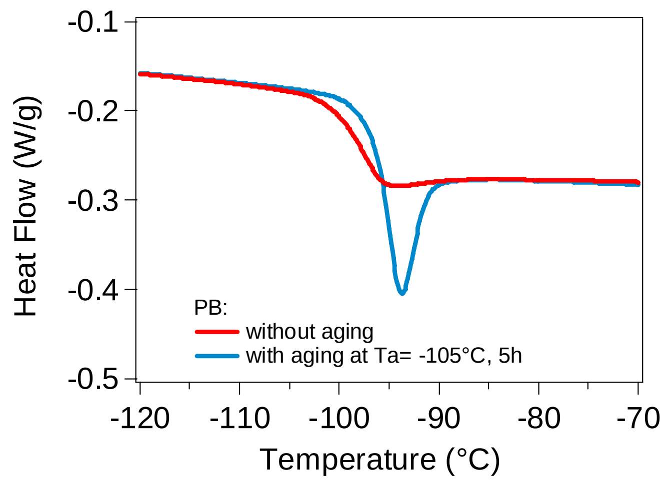
➔ A single and very broadened *Tg* for our blends.

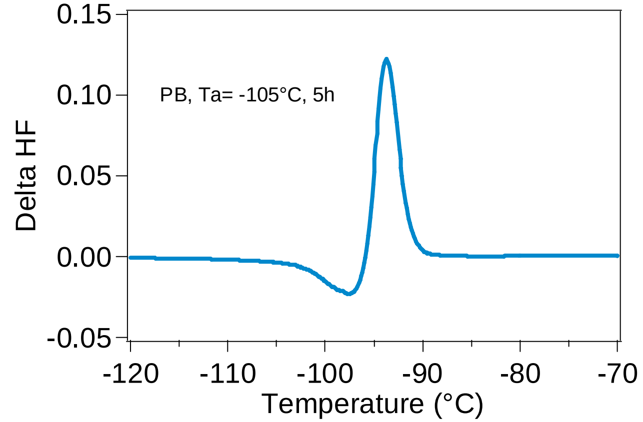
➔ What about physical aging ?

Physical aging of homopolymers

First observation DSC:







Annealing temperature: T_a

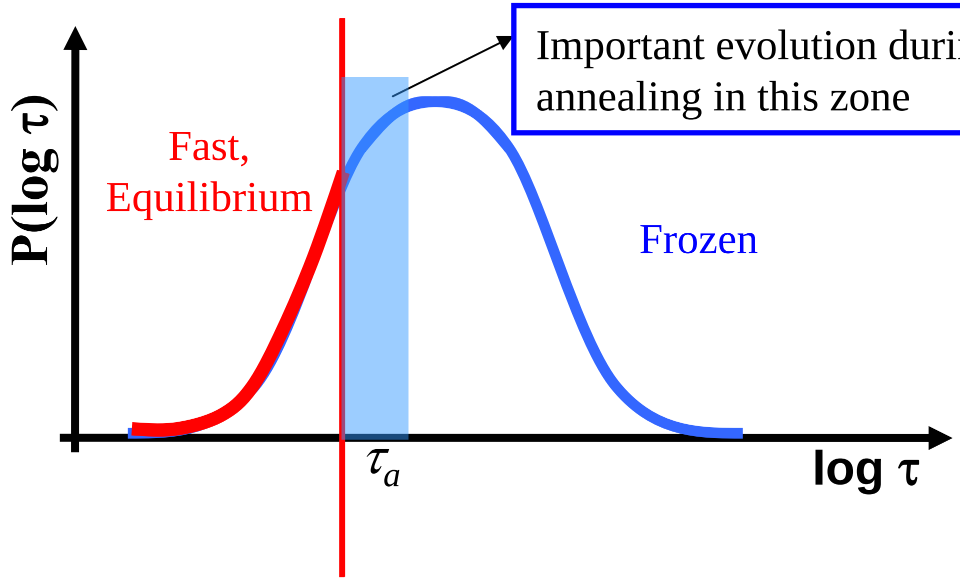
Annealing time τ_a=5h

➔An overshot peak!

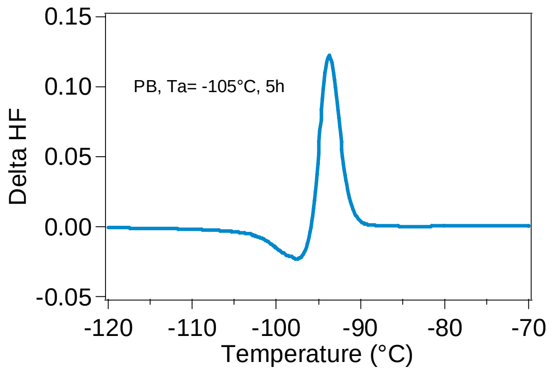
➔Why?

What happened during annealing?

At a given *Ta*



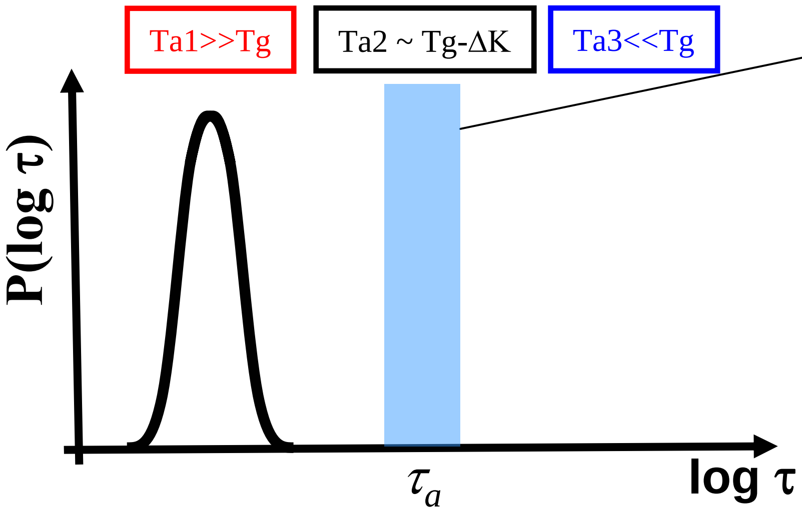
Evolving towards longer relaxation times.
Minima energy landscape.



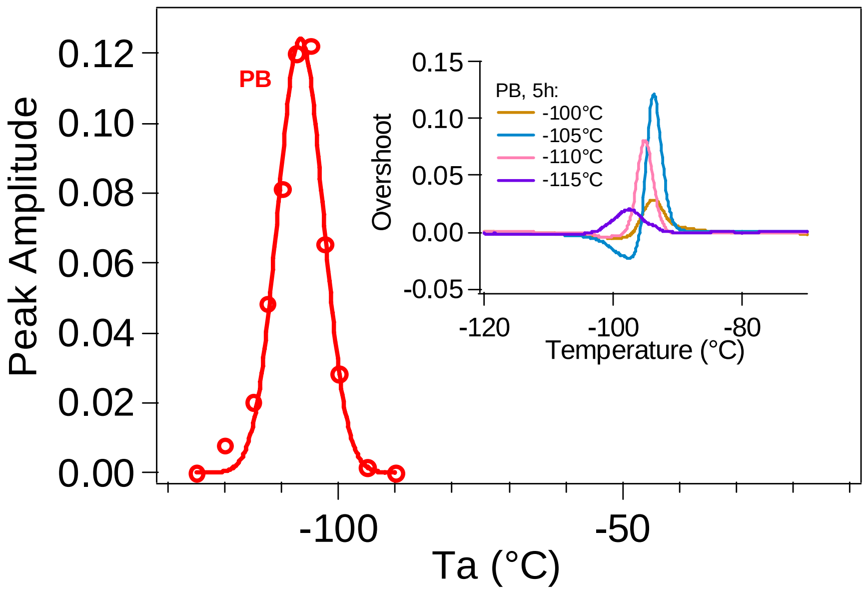
➔Origin of the overshot peak.

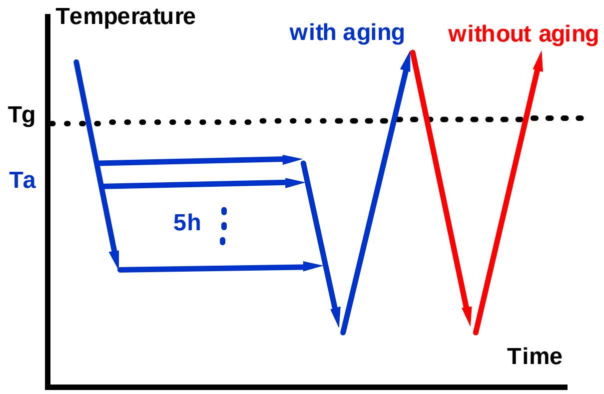
➔If we change Ta??

Physical aging of homopolymers



Important evolution during annealing in this zone

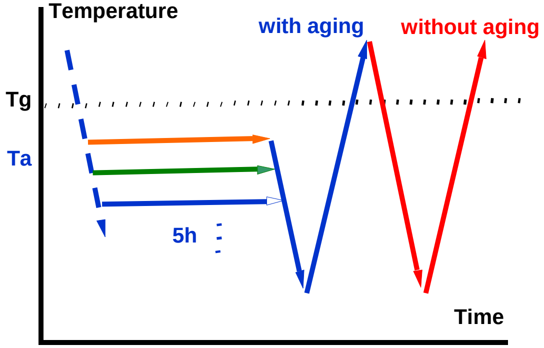


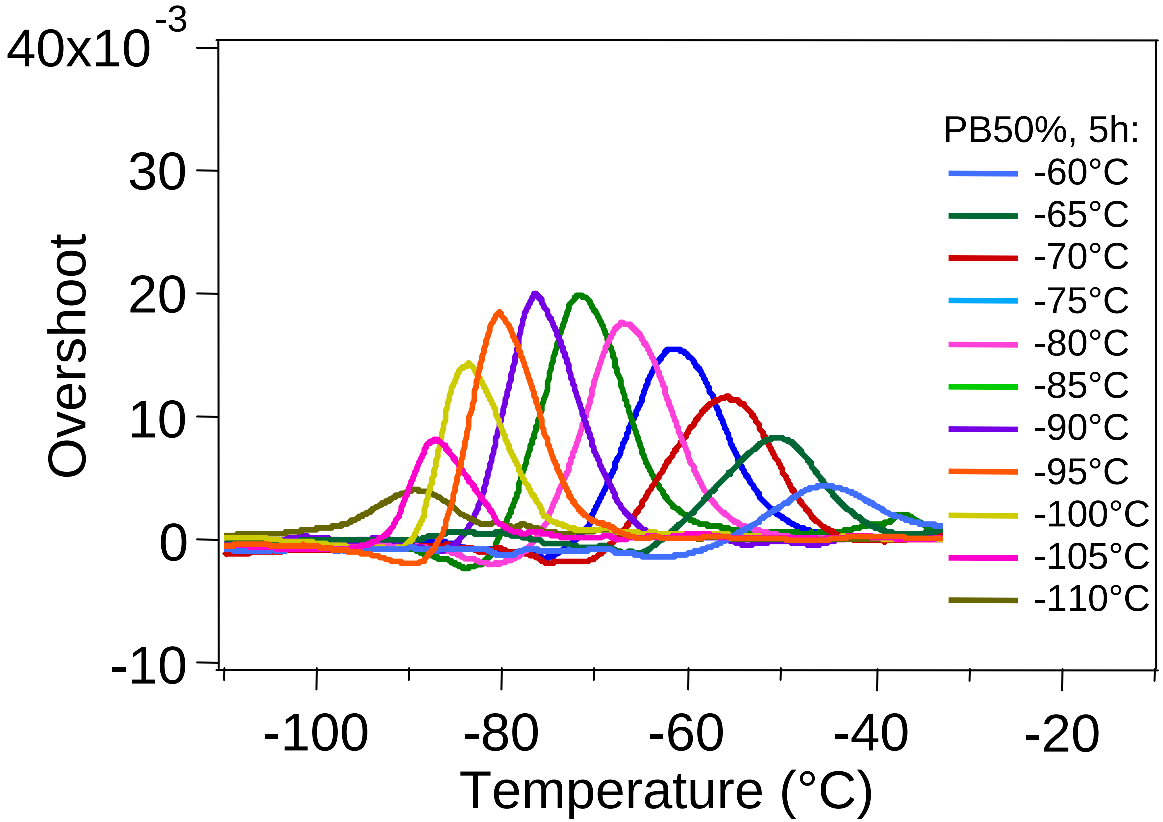


- Narrow distribution of *P(log τ)* or *P(Tg)*
- The overshot position ~ *Tg*.

➔ For blends??

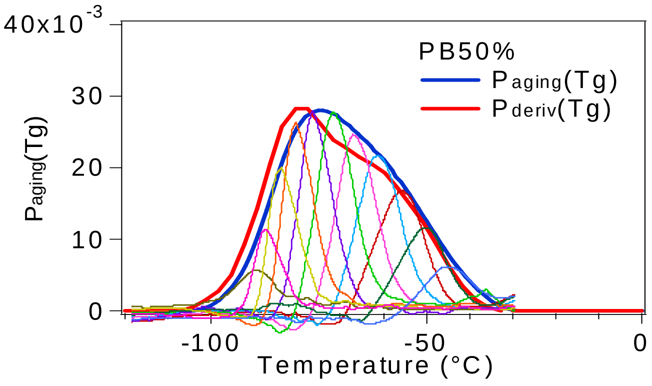
Physical aging of blends



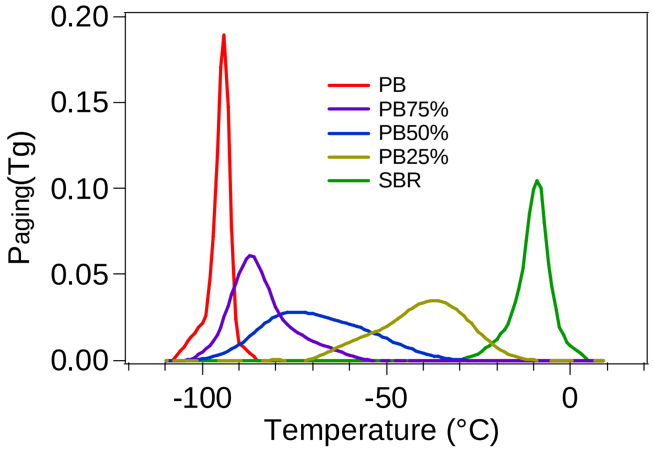


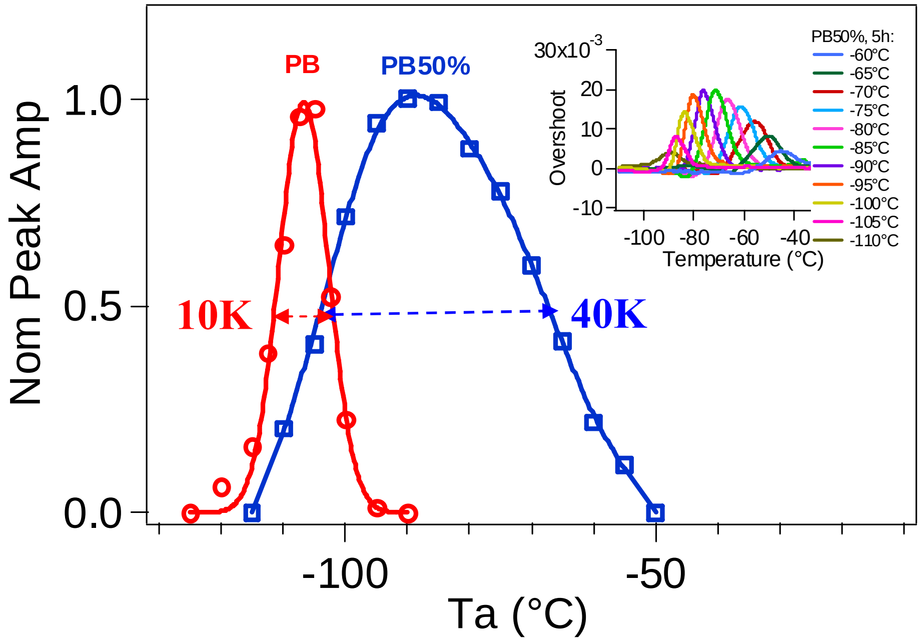
A broad distribution of overshoot peaks ➔ broad *P(Tg)* ??

Physical aging of blends



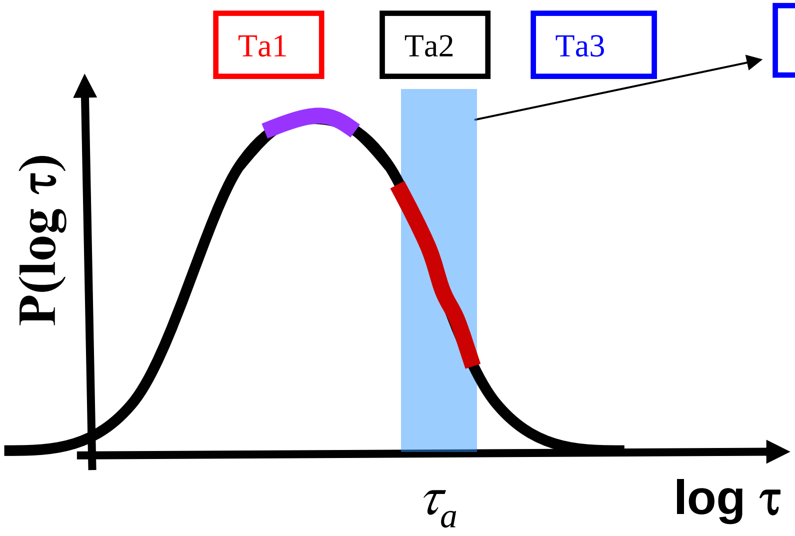
The envelop ~ $P_{aging}(Tg)$ ~ $P_{deriv}(Tg)$





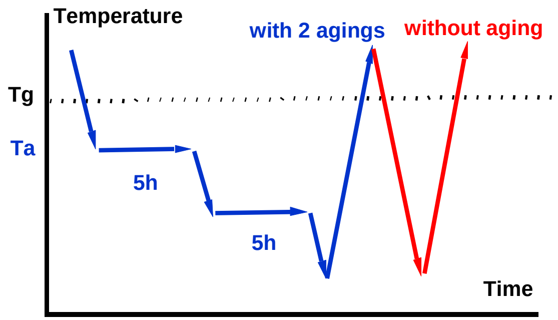
- Broad distribution of *P(Tg)*
- Different domains are selected??

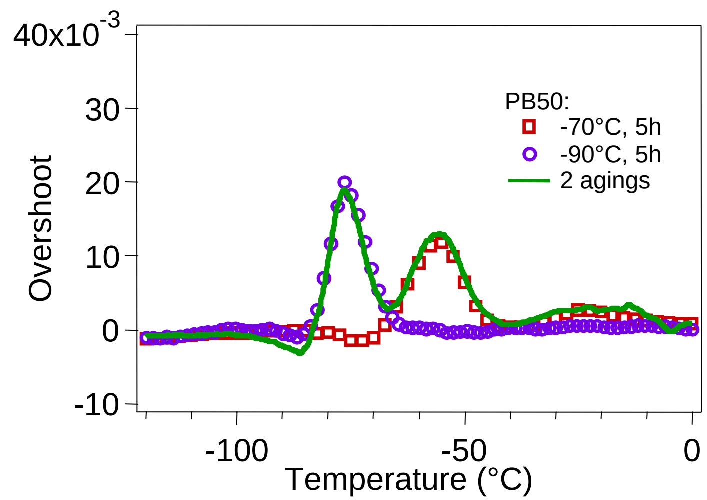
Physical aging of blends



Important evolution during annealing in this zone

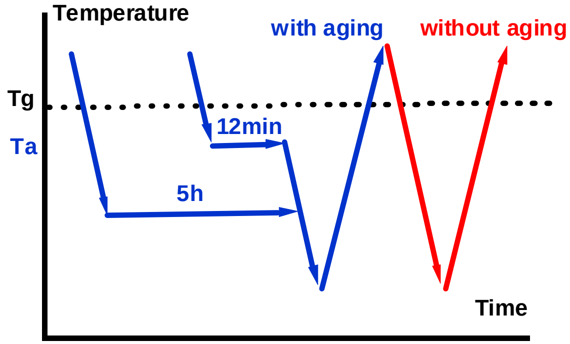
2 consecutive aging temperatures??





➔Each aging overshoot is controlled <u>independently</u> by a corresponding T_a

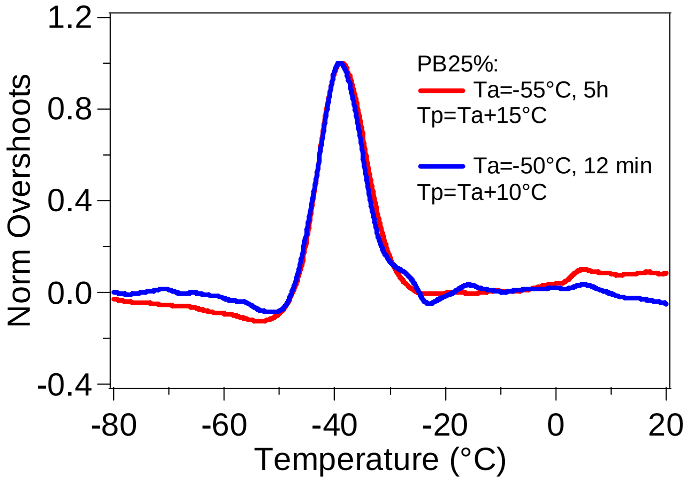
T_a-τ_a superposition

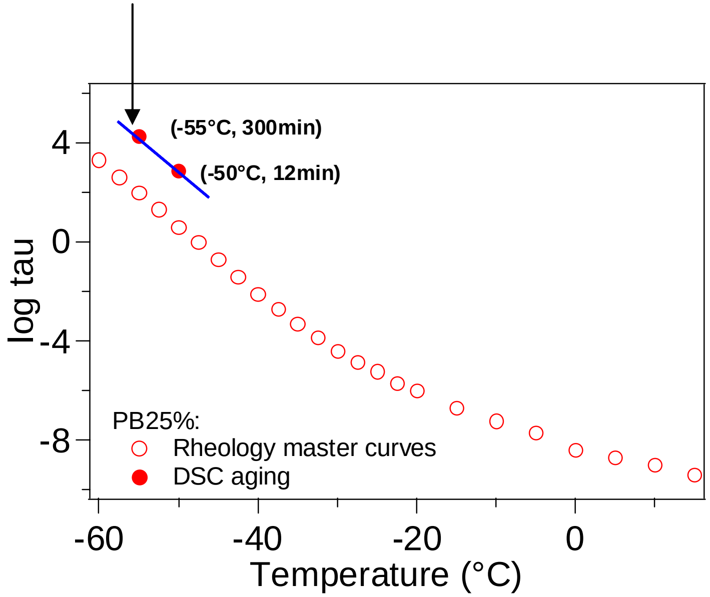


T_a- τ_a superposition…

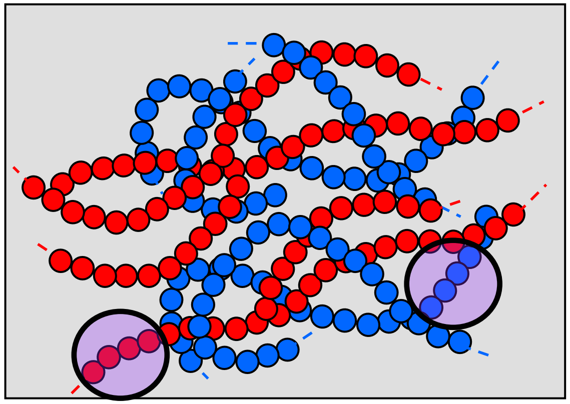
(-55°C, 5h) ~ (-50°C, 12min)

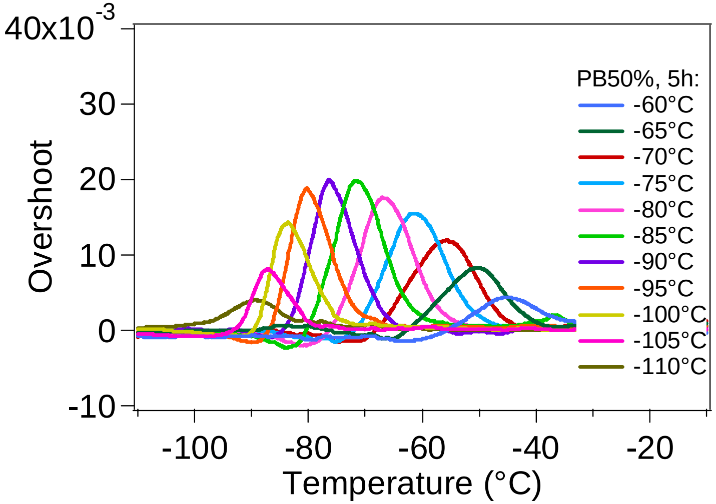
Same slope ➔ similar time temperature superposition law as rheology (WLF)





Physical aging measurement



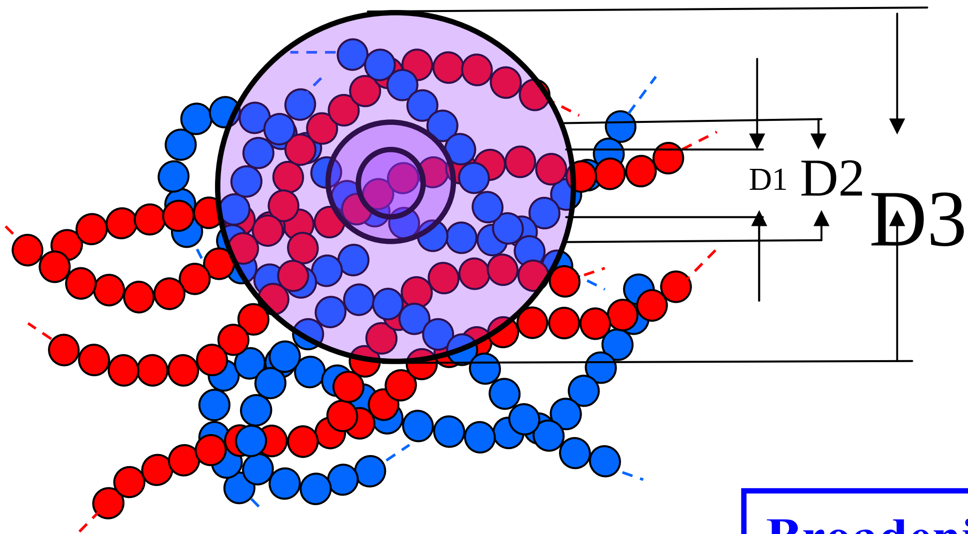


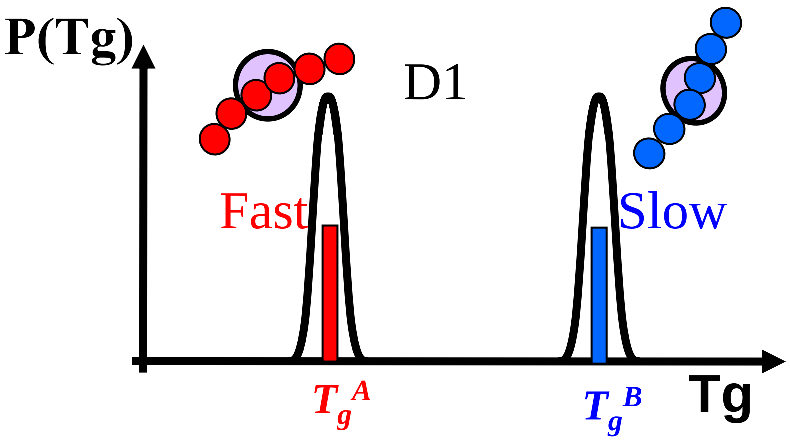
Conclusion 1:

- DSC measurement with physical aging at different T_a exhibits a peak that reveals the independent contribution of different domain of T_g.
- The τ_a-T_a superposition seems to be valid, and is similar to rheology t-T superposition.
- The envelop ~ $P_{aging}(Tg)$ ~ $P_{deriv}(Tg)$

➔ The size scale of the glass transition domain??

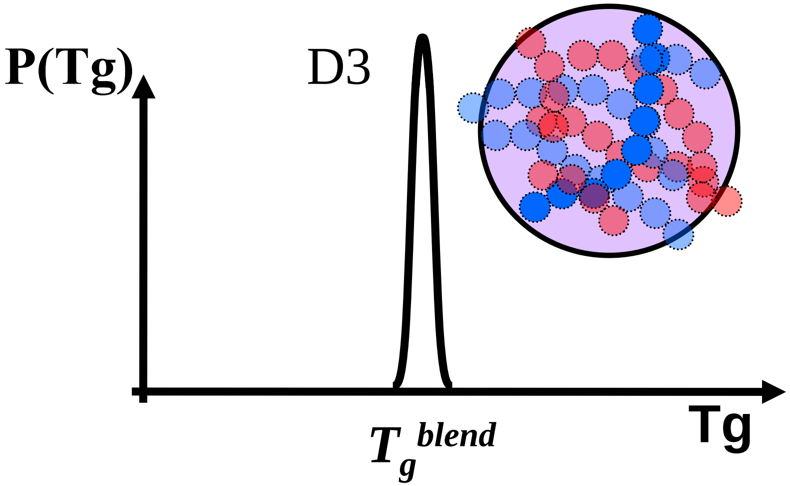
The size scale *D*

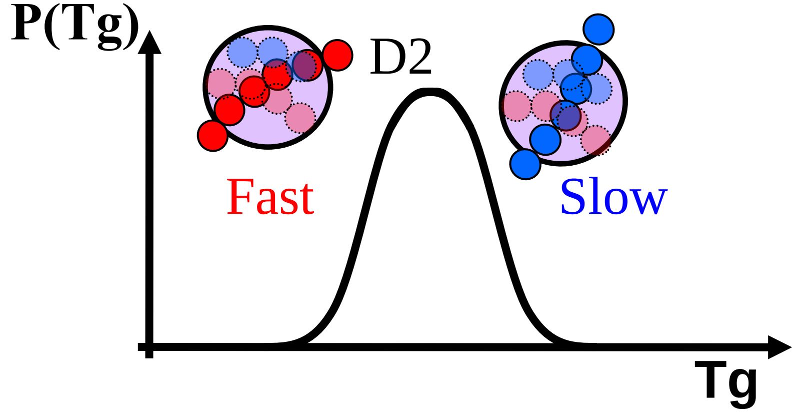




Broadening ∞ 1/D

$$\frac{1}{T_g(\varphi)} = \frac{\varphi}{T_g^{PB}} + \frac{1-\varphi}{T_g^{SBR}}$$





The size scale *D*

Estimation of a characteristic size scale D using Lodge & McLeish + Shenogin & Colby method, we got **ξ~1nm** (a typical value).

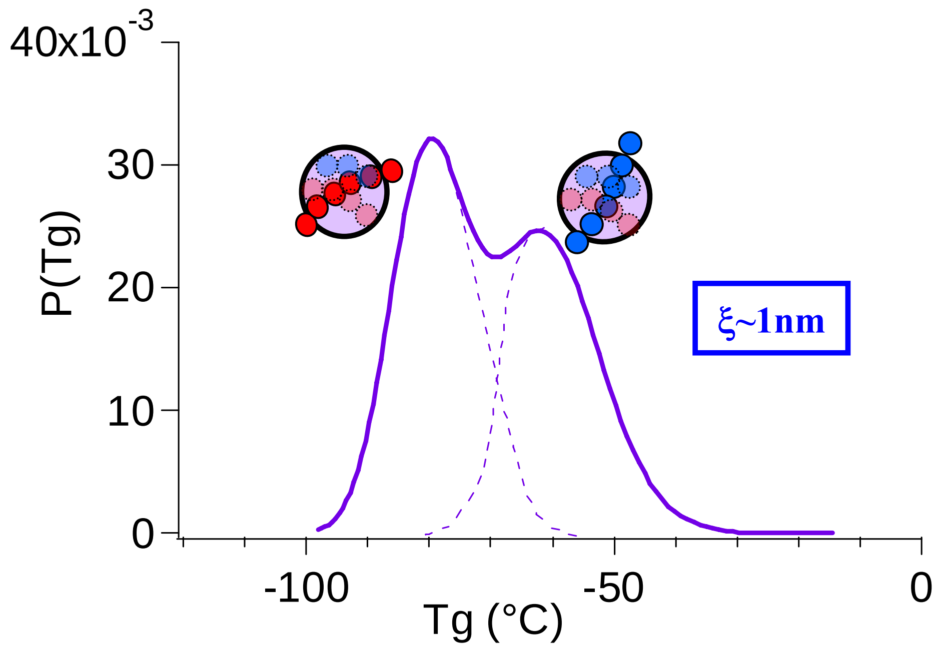


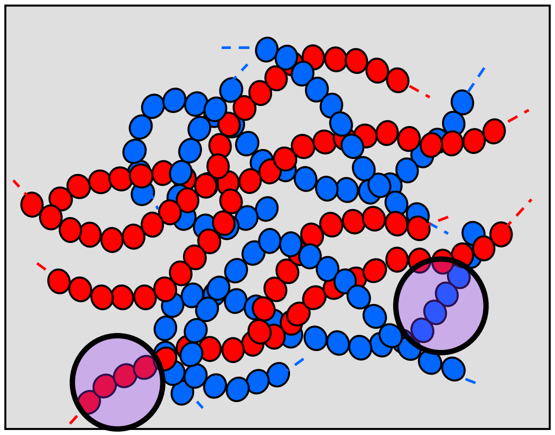
Table 2. Average Values of Correlation Radius and Respective Values of Self-Concentration, Found from the Fits of Eq 20 to the Dielectric Relaxation Data[a]

components	R_c (Å)	ϕ_{self}	T_g (K)
PI	4	0.78	210
PVE	8	0.29	273
PBO	4.3	0.51	200
PVE-89	8	0.29	269
PVME	5.4	0.57	249
PS	~25	0.053	379
P2ClS	16	0.13	402

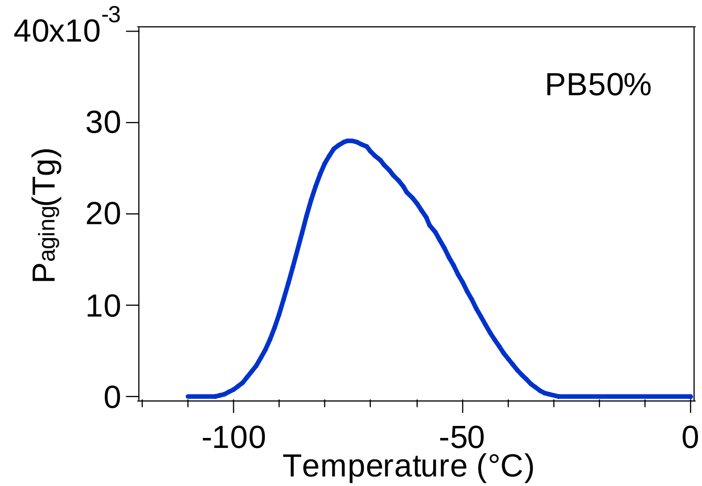
[Shenogin et al., 2007]

Conclusion 2: Our blend system can be considered as an ensemble of domains with different glass transition temperature, and the size scale is ~ 1nm.

Rheology prediction



DSC →

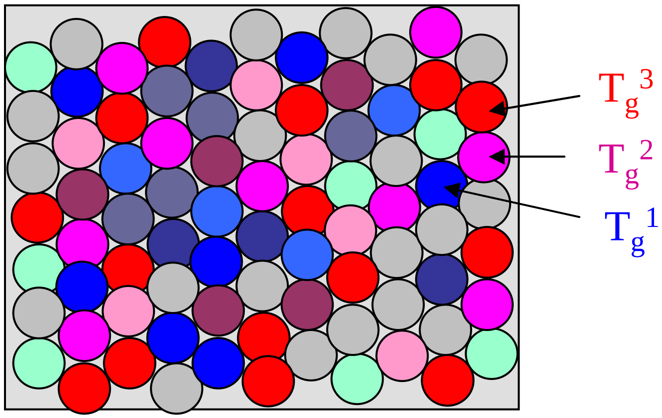


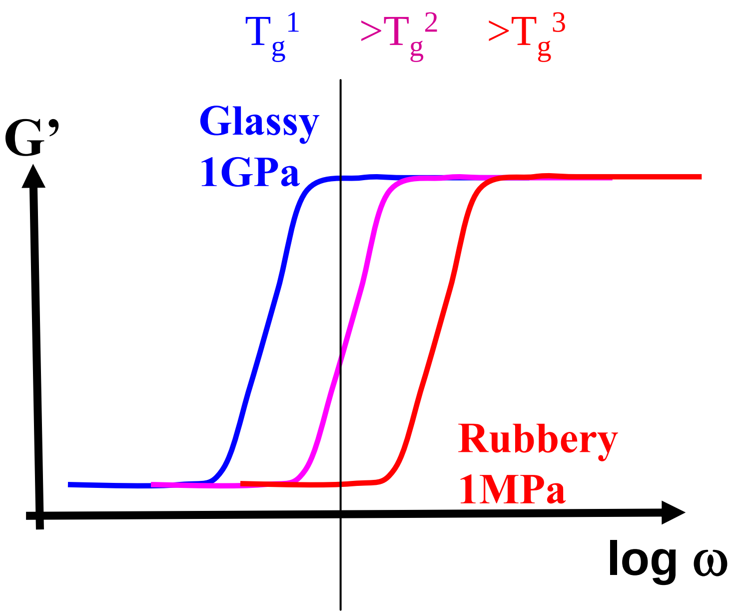
Rheology? →

➔ Is the rheology property controled by the same size scale, and the same Tg distribution??

Rheology prediction

P(log τ) or *P(Tg)*





Viscoelastic spectra of a local domain of $G^*(Tg)$:

WLF law + modified Havriliak Negami function

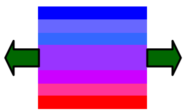
$$G^* = G_{glass} - \frac{G_{glass} - G_{rub}}{\left(1+\left(j\omega\tau_{HN}\right)^{\alpha}\right)^{\beta}}$$

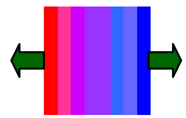
All the parameters are interpolated from pure polymers at various local *Tg*

G'_{macro} = average of G'_i

➔ HOW??

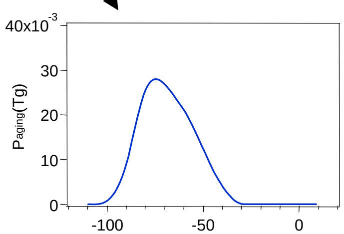
Parallel or in-series?





$$G^*_{//} = \int G^*(T_g) P(T_g) dT_g$$

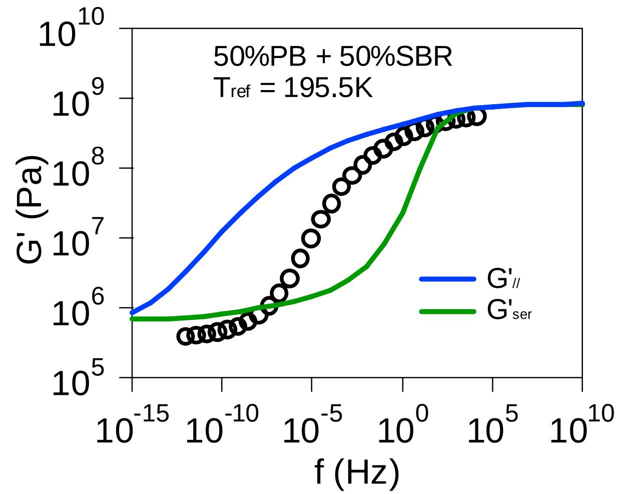
$$\frac{1}{G^*_{ser}} = \int \frac{P(T_g)}{G^*(T_g)} dT_g$$

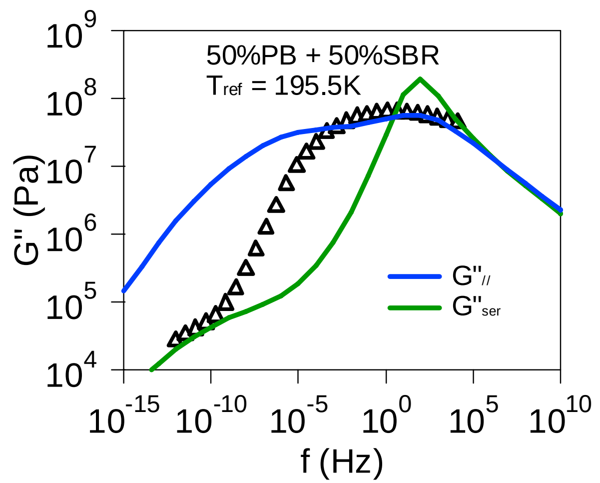


distributions from $P_{aging}(Tg)$

➔ Neither the parallel nor the series averaging is able to give a correct description.

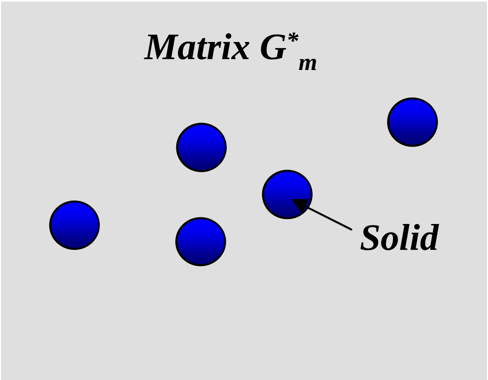
➔ Need for a more refined model.

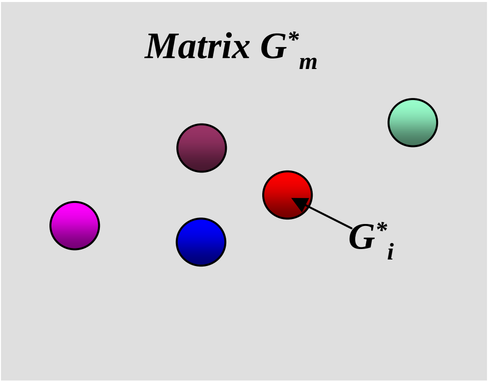


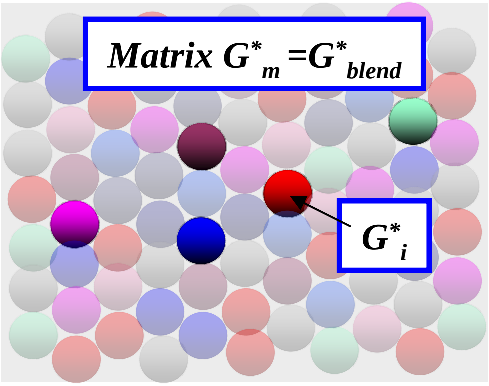


Rheology data: master curves

Rheology prediction







Dilute solid particle-filled system:

$$G^* = G^*_m \left(1 + \frac{5}{2}\Phi\right)$$

Volume fraction

Einstein equation.

[Einstein, 1911]
[Smallwood, 1944]

Dilute visco-elastic inclusions:

$$G^*_{blend} = G^*_m \left(1 + \frac{5}{2}\sum_i f_i H_i\right)$$

$$H_i = \frac{2G^*_i - 2G^*_m}{2G^*_i + 3G^*_m}$$

Volume fraction

Olroyd-Palierne model.

[Palierne, 1990]

Heterogeneous visco-elastic system:

$$\sum_i f_i H_i = 0$$

$$H_i = \frac{2G^*_i - 2G^*_m}{2G^*_i + 3G^*_m}$$

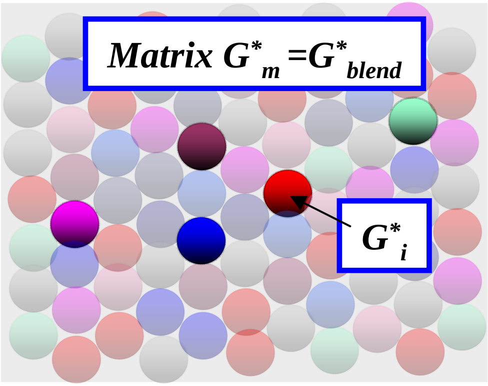
Self-consistent Olroyd-Palierne model.

[Lequeux, 2001]

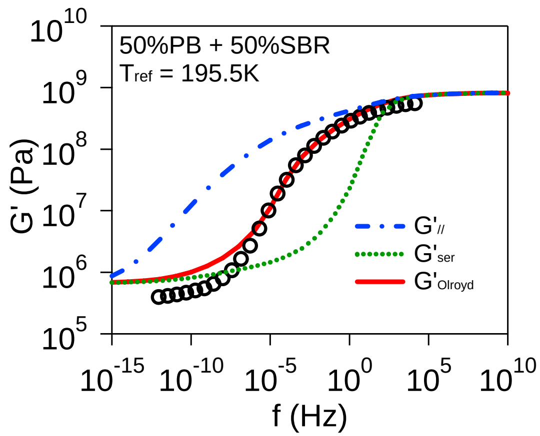
Self-consistent Olroyd-Palierne model

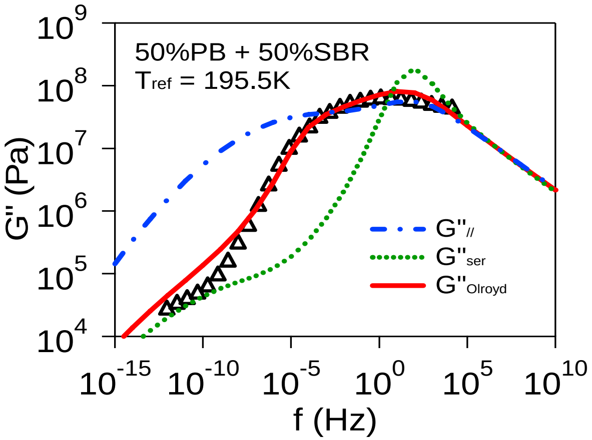
- Self-consistent Olroyd-Palierne model : *[Lequeux, 2001]*

$$\int \frac{2G^*(T_g) - 2G^*_{blend}}{2G^*(T_g) + 3G^*_{blend}} P(T_g)\, dT_g = 0$$



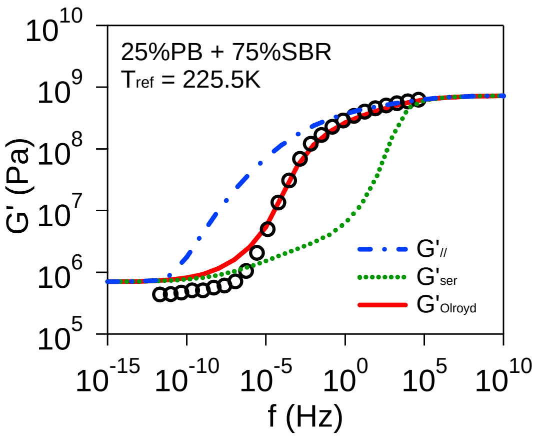
Spherical inclusions Gi with volume fraction fi

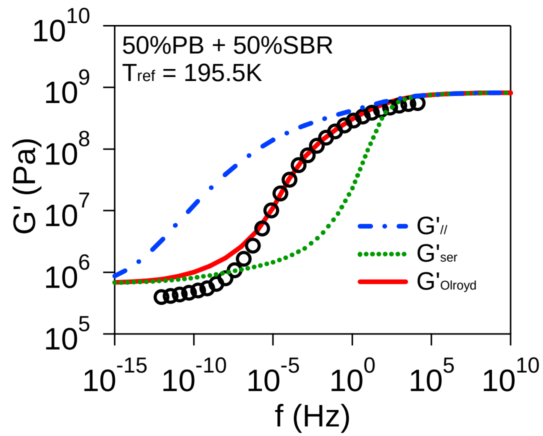


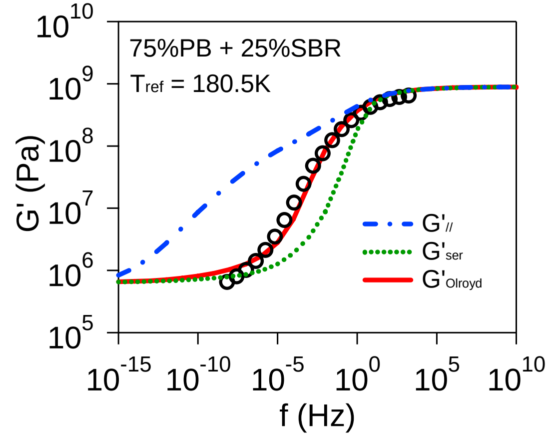


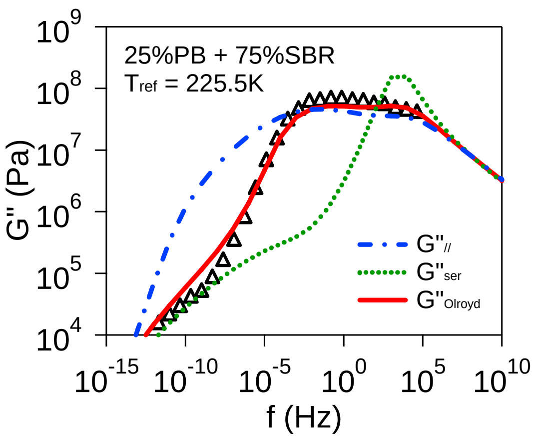
- Agreement!!
- Prediction of blend's rheology from DSC measurements and pure polymers' rheology.
- No adjustable parameters.

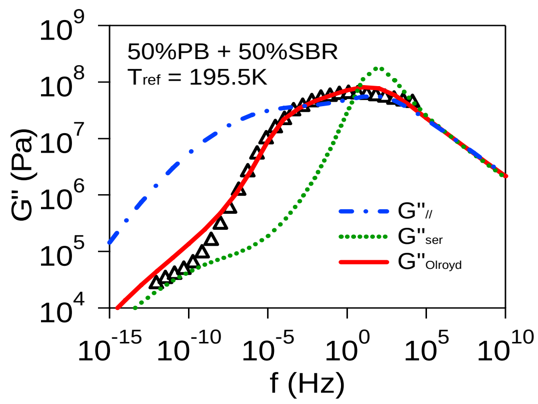
Self-consistent Olroyd-Palierne model

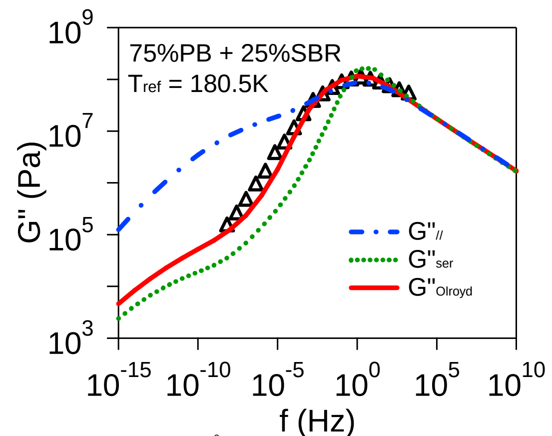


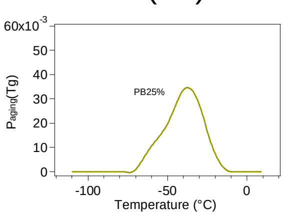


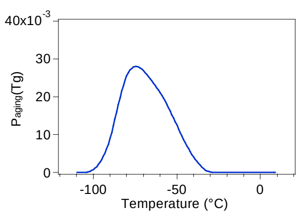


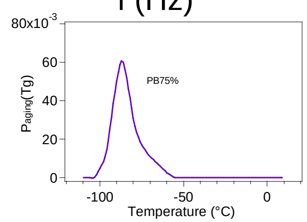




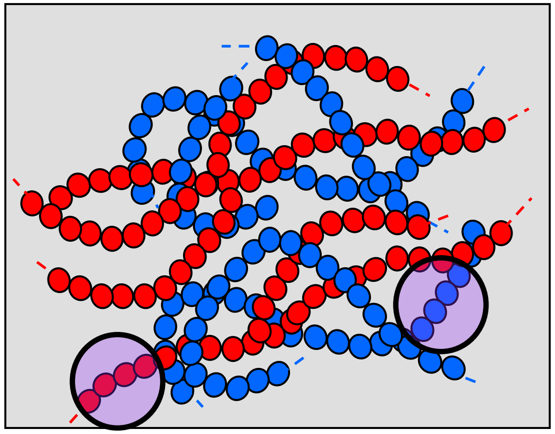






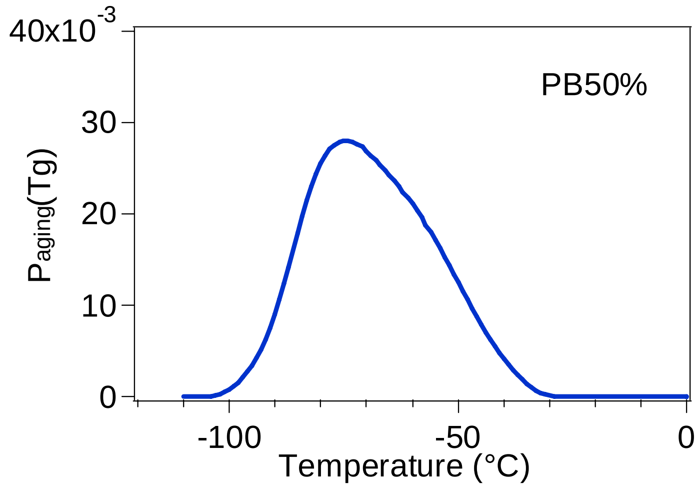


Rheology prediction



DSC

Aging

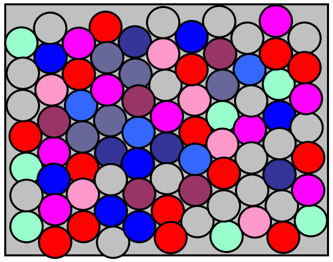


Rheology:OK!

Conclusion 3:

- The rheology property of our blend is controled by the same size scale (1nm), and the same Tg distribution.
- Our blend system can be considered in its glass transition regime as an arrangement of independent viscoelastic domains, each one with a specific glass transition. The best way to average viscoelastic moduli in such heterogeneous system, is the self-consistent Olroyd-Palierne model.

General Conclusions



- **Physical aging** of our blend system occurs independently at domains of a scale ~ 1nm.

- The **rheology** property of our blend system in its glass transition regime can be regarded as an ensemble of independent viscoelastic domains of a scale ~ 1nm.

- Open question: is it general for polymer blends?

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Thank you!