Blending lignins and PBS: impact on thermal stability

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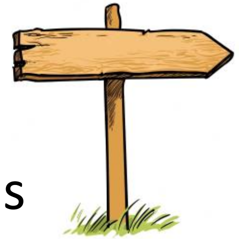
Outline

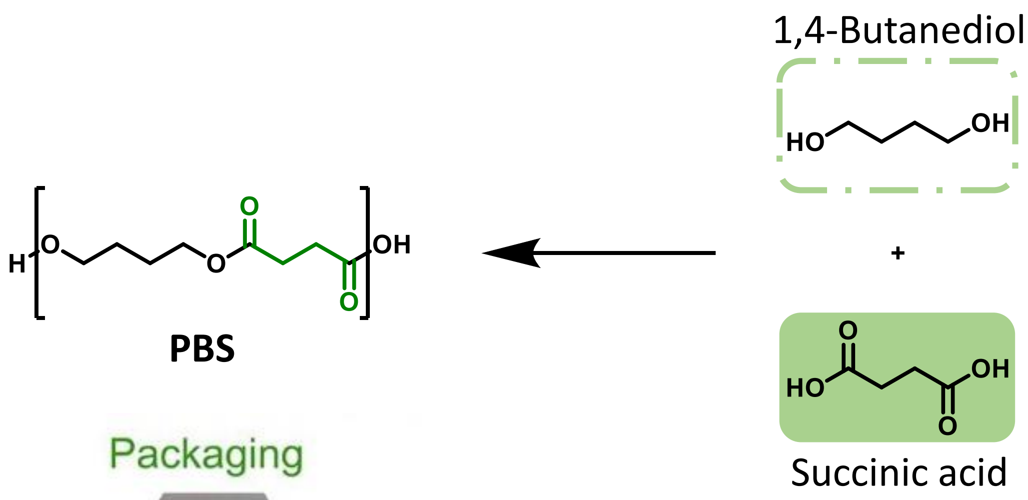
- Intro
  - PBS
  - Lignins

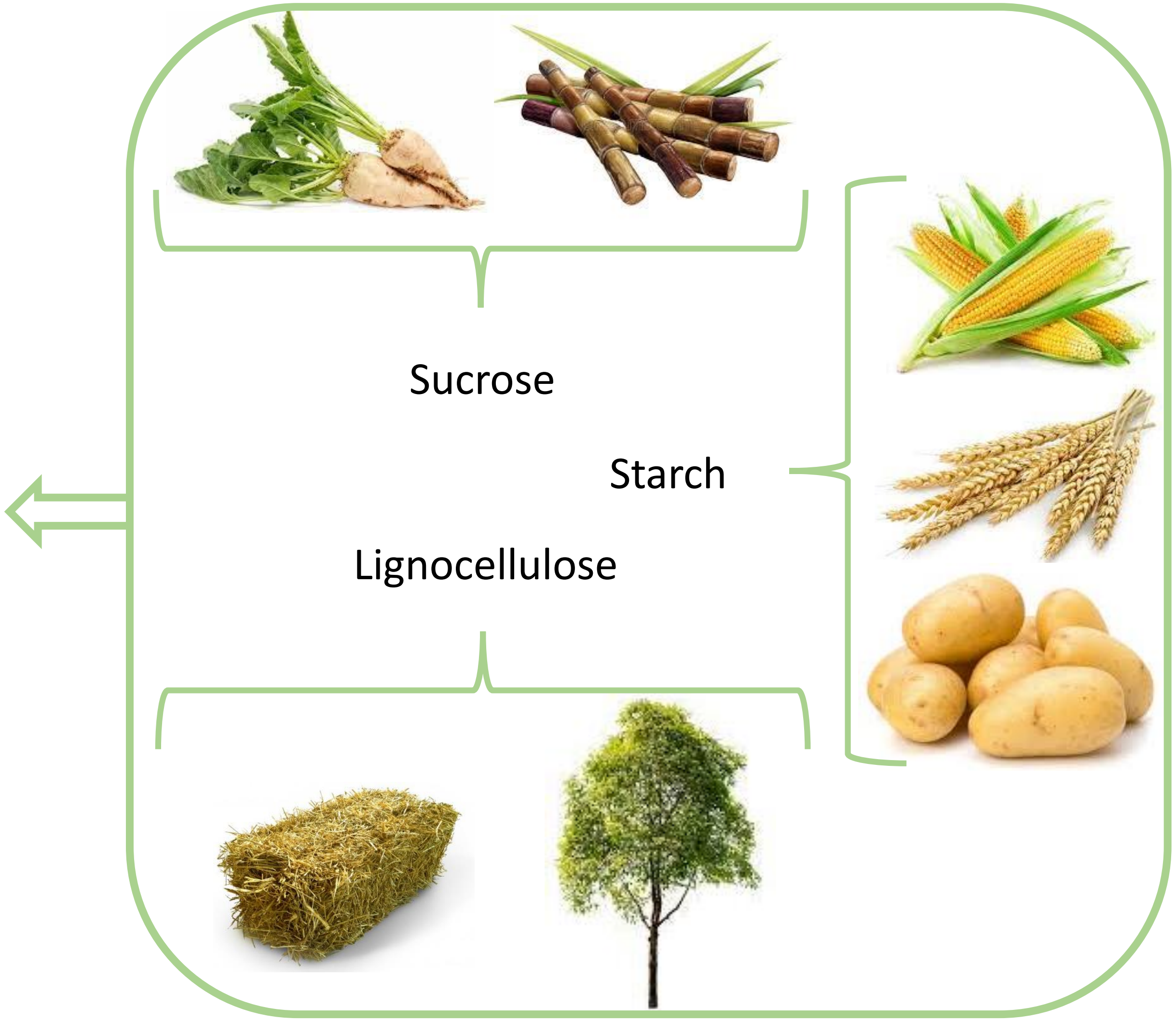


- Samples preparation
  - Blending PBS and lign
  - Film pressing

- Film analysis
  - DSC_N_2
  - TGA
  - DSC OOT
  - DSC OIT
  - …

Intro - Poly(butylene succinate) PBS





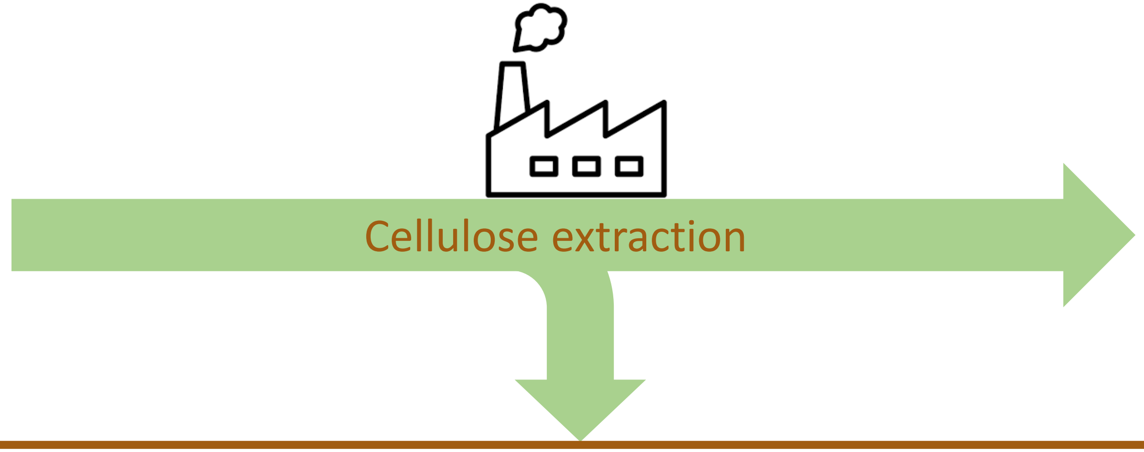
$T_m \approx 115$ °C
$70 < T_c < 90$ °C
$T_g \approx -35$ °C
Density 1.26

Biobased polyester
Biodegradable

Platnieks O. *et al.*,
European Polymer Journal, **2021**.

Intro - Lignins

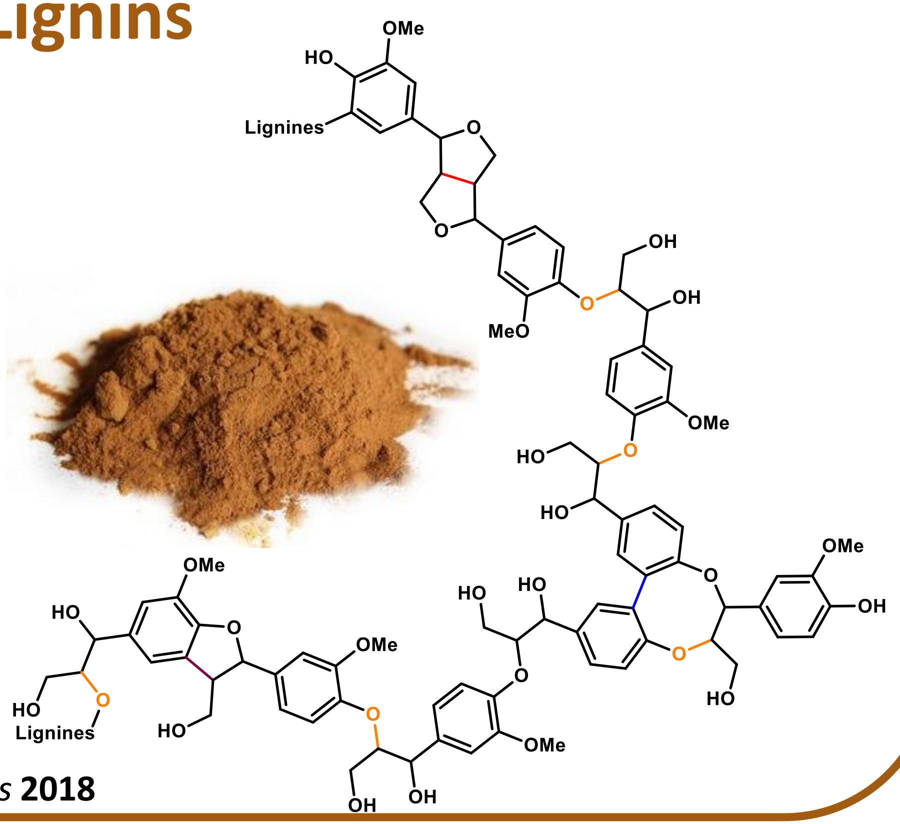
Lignocellulosic biomass



Paper, 2G bioethanol

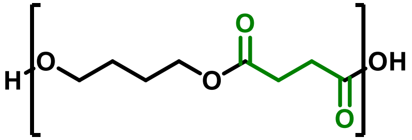
Lignins

- Surround cellulose
- Verticality
- Rigidity
- Anti-UV
- Antiradical
- Antibacterial
- Antifungal



Zhao X. *et al.*, *Polymers* **2018**

Intro - Lignins as additives in PBS



Bioplastic

+

Biobased additive

Enhanced
biobased composite

- Anti-UV
- Antiradical
- Antibacterial
- Antifungal

+Thermal stability

Active packaging
Biomedial applications

Processability

Specific properties of interest
Unvalorised biobased by-product

Samples preparation

Samples preparation - Blending PBS and lignins

Commercial **PBS**

Commercial soda **lignins**
1, 2 or 3%wt.

Internal mixer conditions:
at 140°C,
100 rpm,
5 min

Lab-made resulting blends

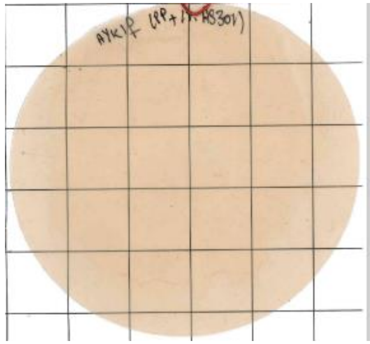
Blends of various lignins content

Samples preparation - Film pressing

Pressing conditions:
at 140°C,
1.5 kN for 3 minutes,
100 kN for 3 minutes,
Cooling

0%

1%



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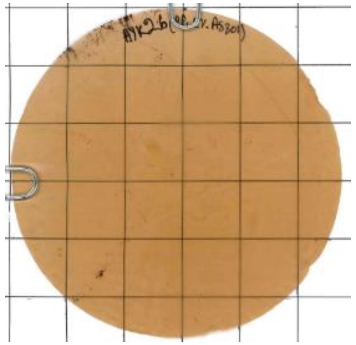

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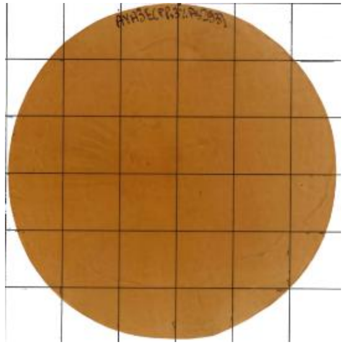


Lab-made resulting films
150 µm x 15 cm
Different lignins loads

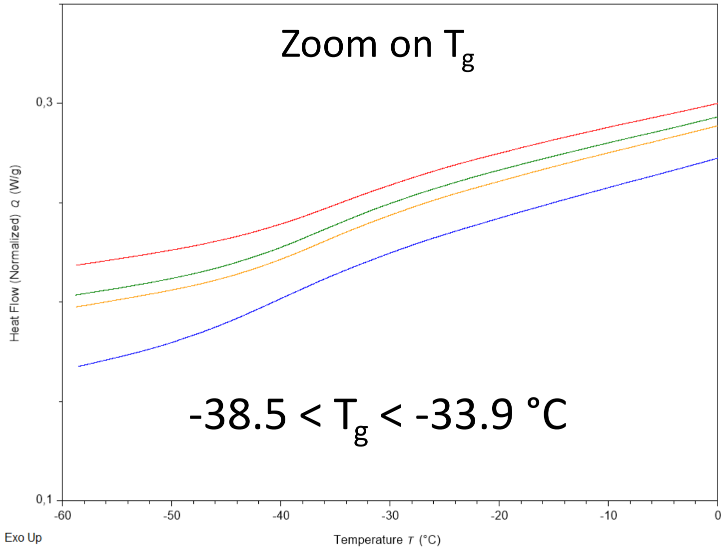
Impact of lignins on film properties?

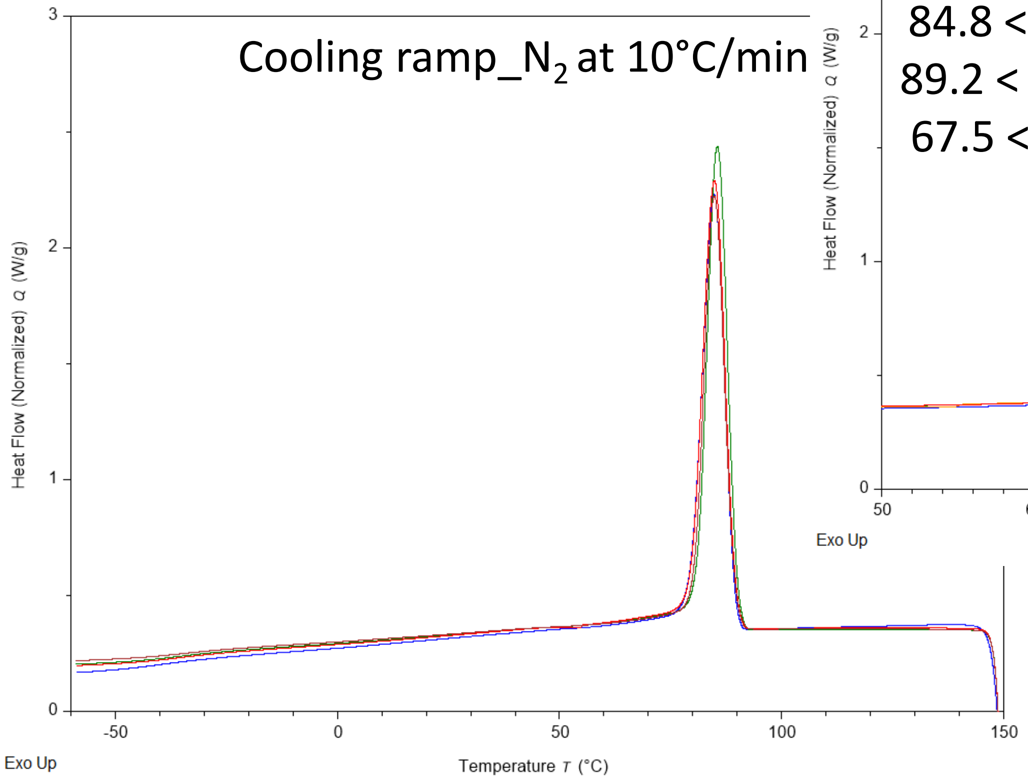
Film analysis

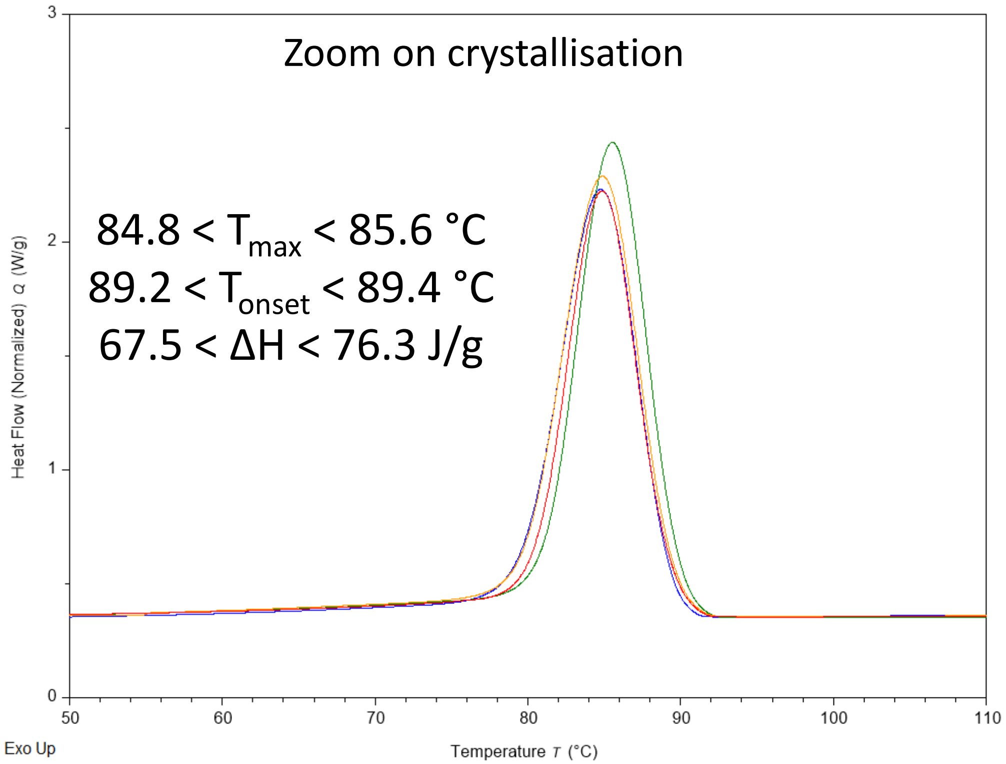
Films analysis - DSC_N_2, cooling

PBS
PBS + 1%Lignins
PBS + 2%Lignins
PBS + 3%Lignins

5 mg ± 0.5,
From 150 to -60 °C,
At 10 °C/min,
N_2





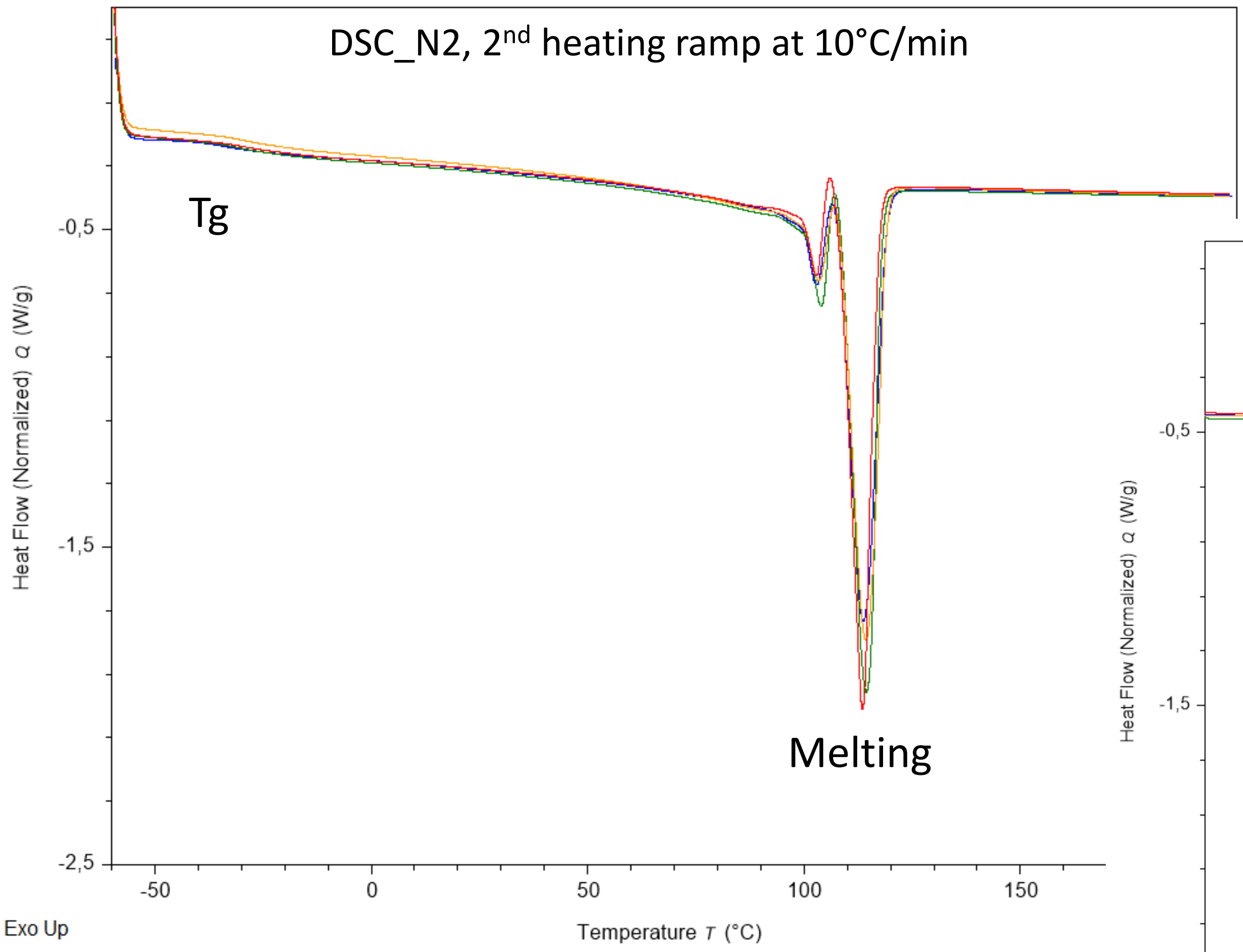


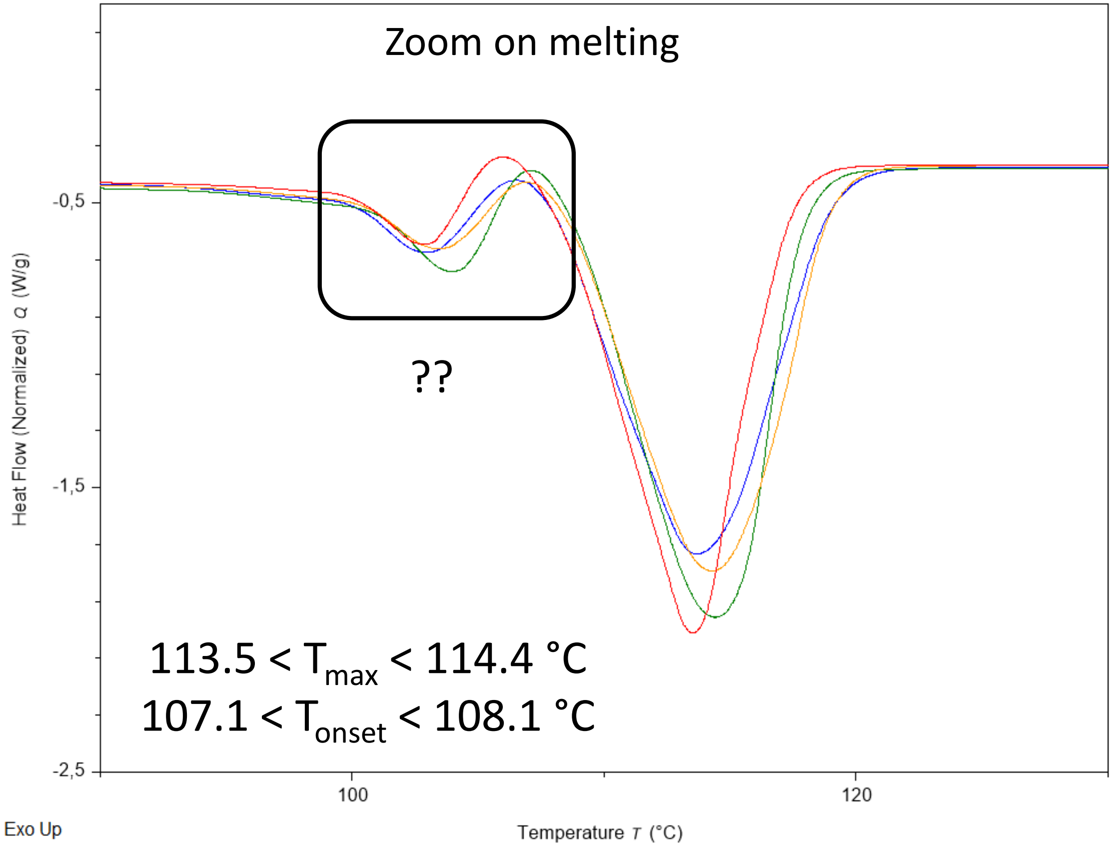
Low/no impact of lignins addition on T_g and crystallisation behaviour in these conditions

Films analysis - DSC_N_2, 2nd heating

PBS
PBS + 1%Lignins
PBS + 2%Lignins
PBS + 3%Lignins

5 mg ± 0.5,
From -60 to 200 °C,
At 10 °C/min,
N_2



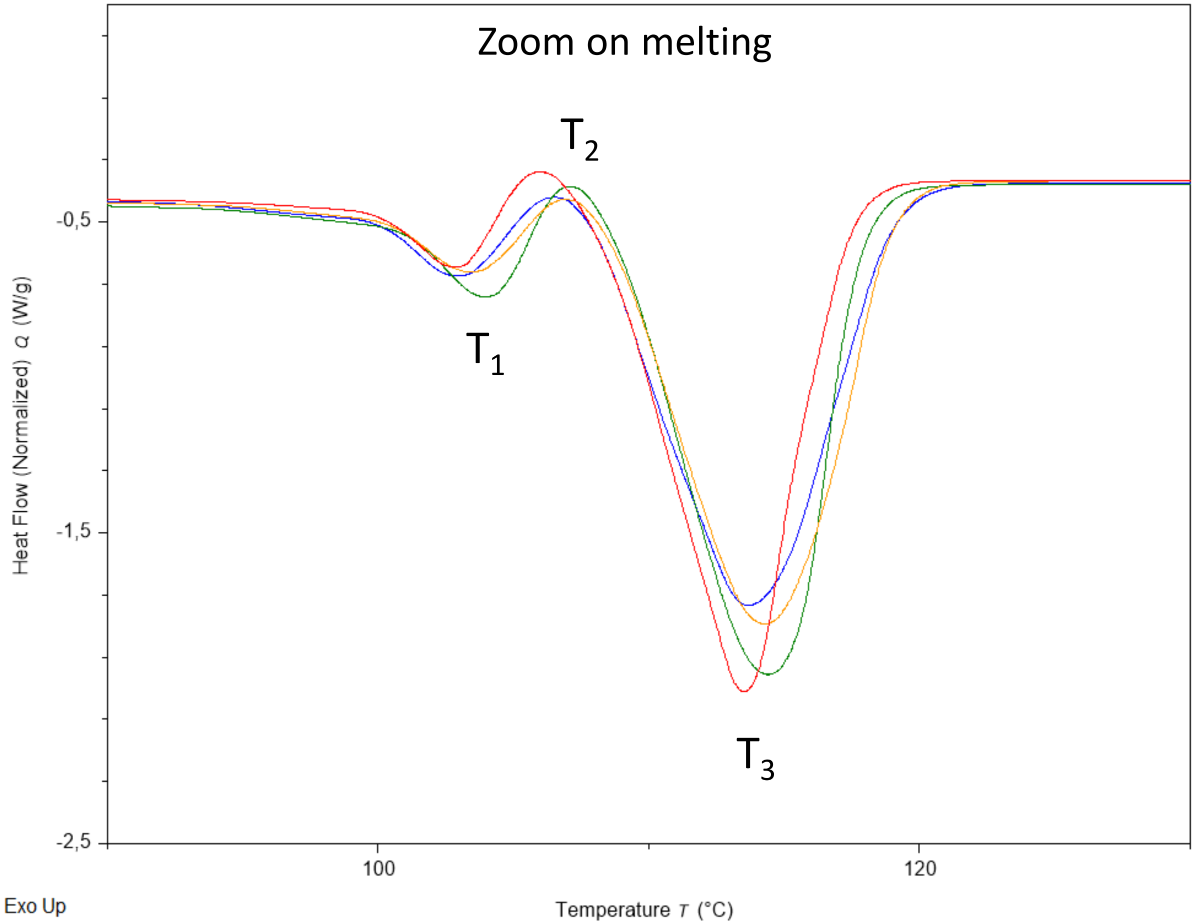


No significant impact of lignins on melting behavior
Why a « double peak »?

Films analysis - DSC_N_2, 2[nd] heating

PBS
PBS + 1%Lignins
PBS + 2%Lignins
PBS + 3%Lignins

5 mg ± 0.5,
From -60 to 200 °C,
At 10 °C/min,
N_2



Melting Behavior of Poly(butylene succinate) during Heating Scan by DSC

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Received 22 September 1997; revised 8 February 1999; accepted 10 February 1999

Isothermal crystallisations
- DSC
- XRD

T_1 = endo = melting of original crystallites
T_2 = exo = melt-recrystallisation
T_3 = endo = melting of recrystallised + original ones

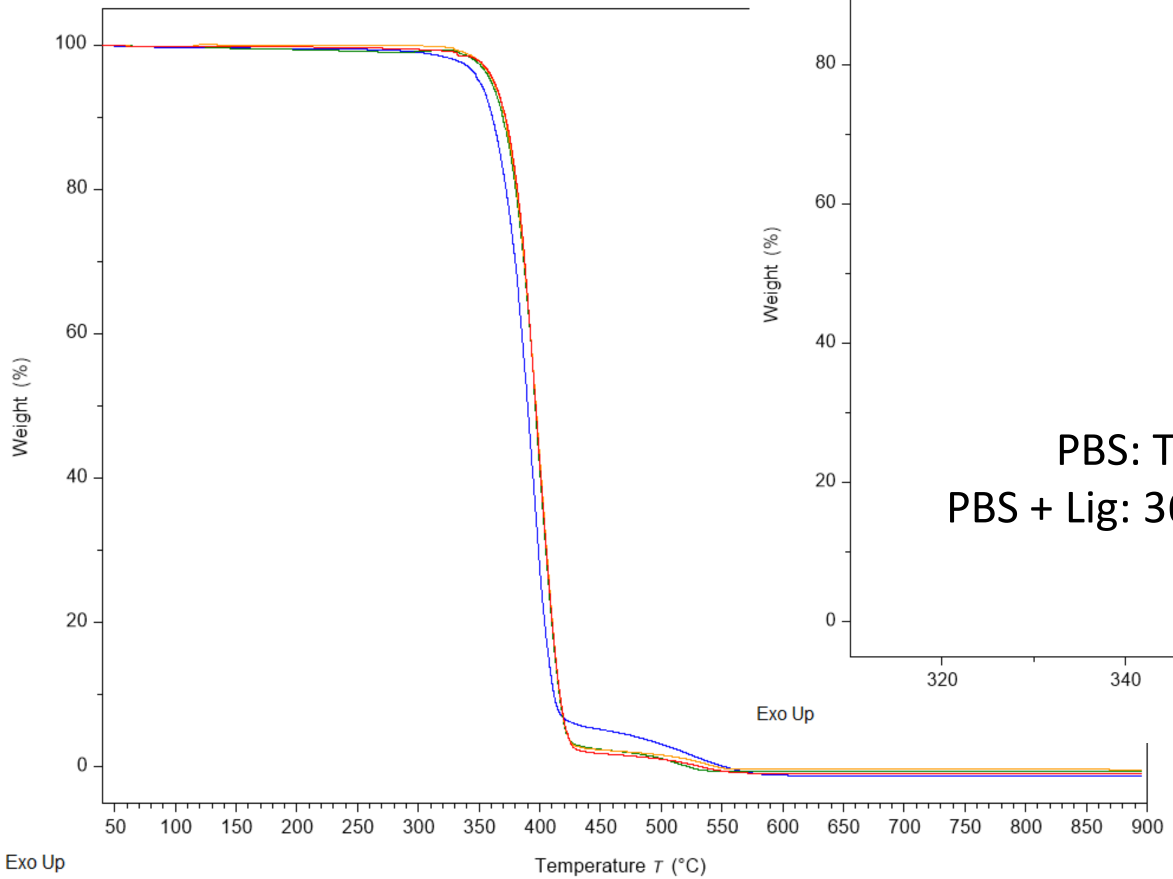
Original melting overlapped with melt-recrystallisation

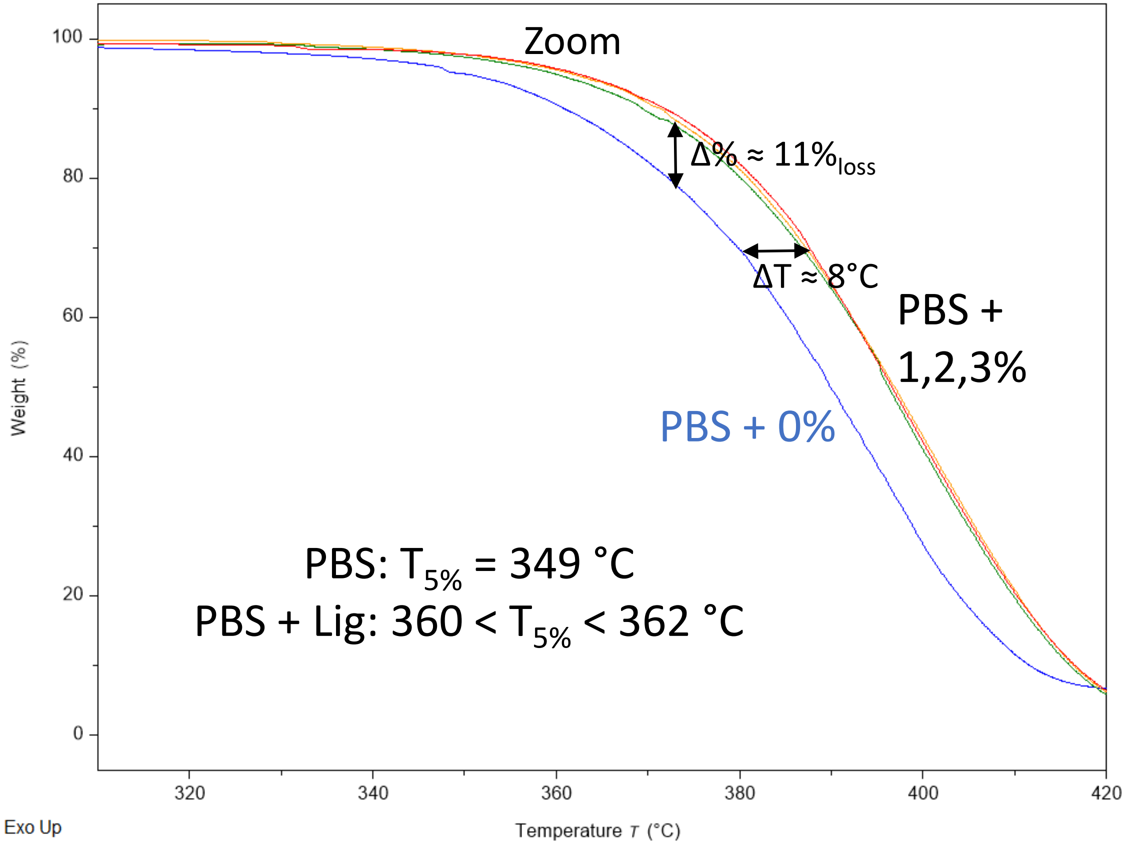
Yoo E.S. *et al.*, *Journal of Polymer Science*, **1999**.

Films analysis - TGA

PBS
PBS + 1%Lignins
PBS + 2%Lignins
PBS + 3%Lignins

17 mg ± 2,
From 40 to 900 °C,
At 10 °C/min,
N_2

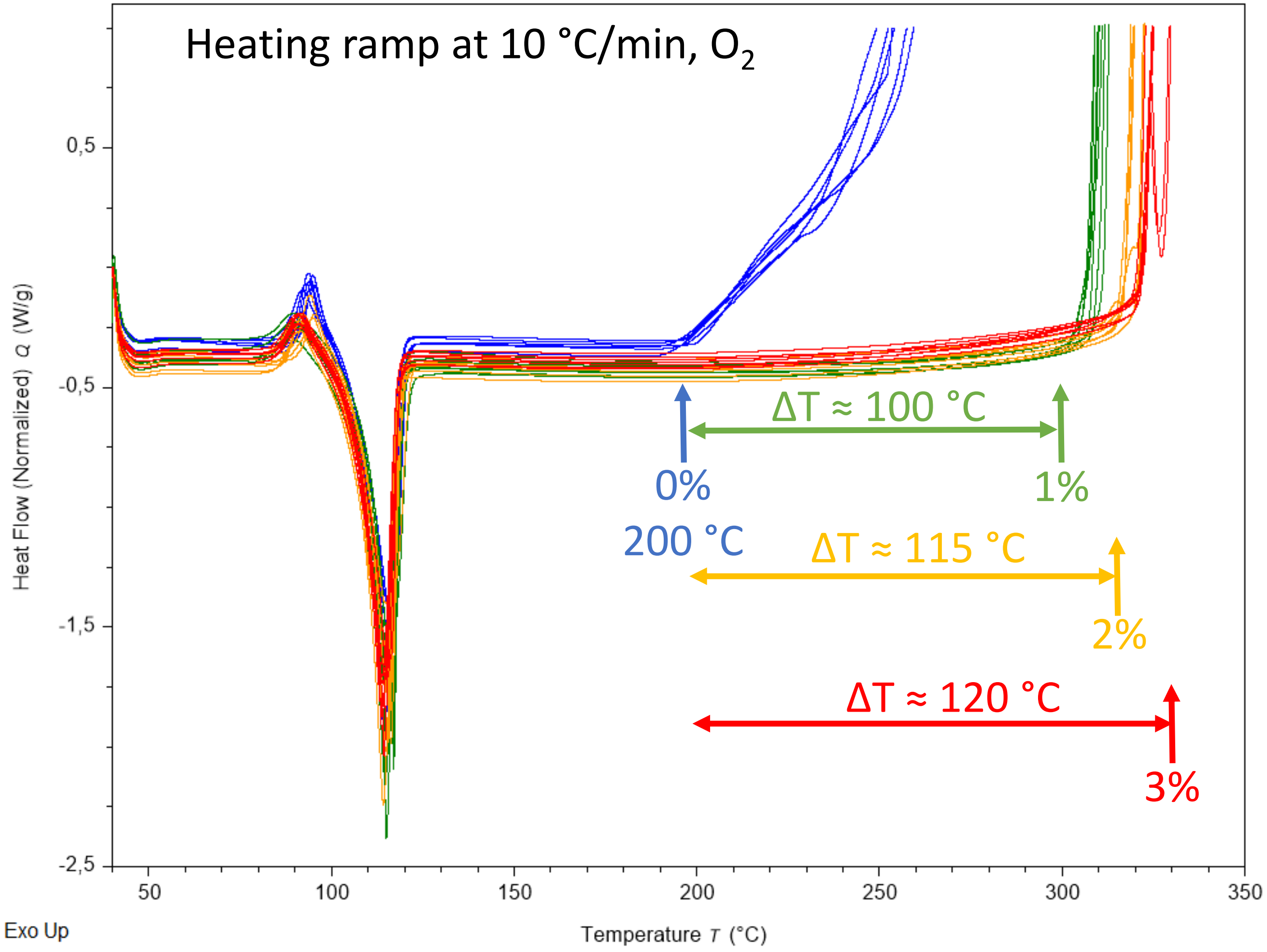




Increase of T_d when lignins added
No influence of %Lignins observed

Films analysis - DSC OOT

OOT = Onset Oxidation temperature



PBS
PBS + 1%Lignins
PBS + 2%Lignins
PBS + 3%Lignins

5 mg ± 0.5,
From 40 to 350 °C,
At 10 °C/min,
O_2 at 50 mL/min

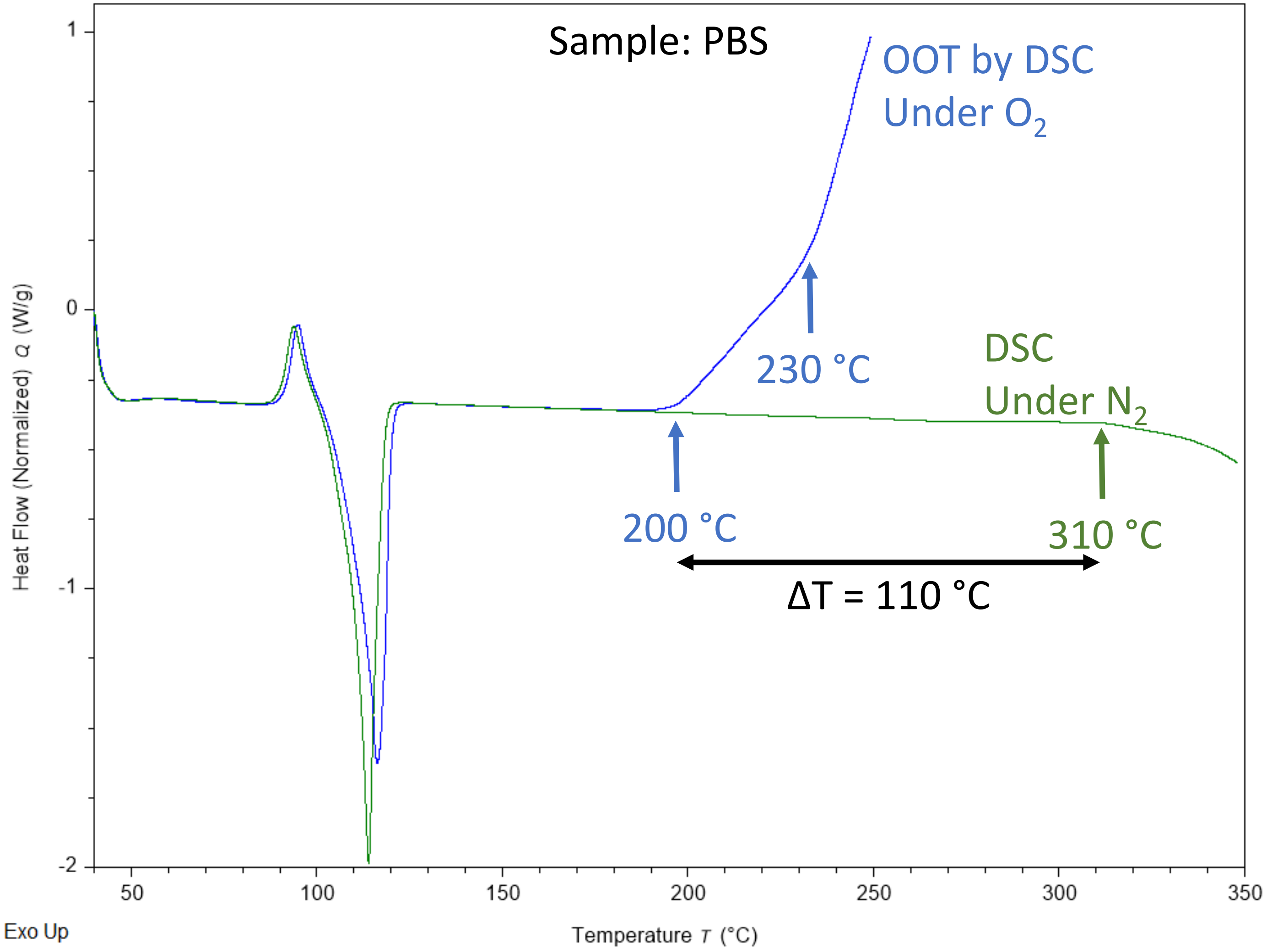
%Lignins	$T_{5\%loss}$ [°C] (TGA_N_2)	OOT [°C] (DSC_O_2)
0%	350	200
1%	360	300
2%	361	315
3%	362	320

PBS + Lignins: sudden exo phenomenon
PBS: 2 steps exo phenomenon
-> Different chemical mechanisms?
-> Auto-acceleration?
-> Nucleation effect inhibited by lignins?

Protective effect of lignins against oxidation
Moderate effect of %Lignins

Films analysis - DSC, comparing OOT vs N_2

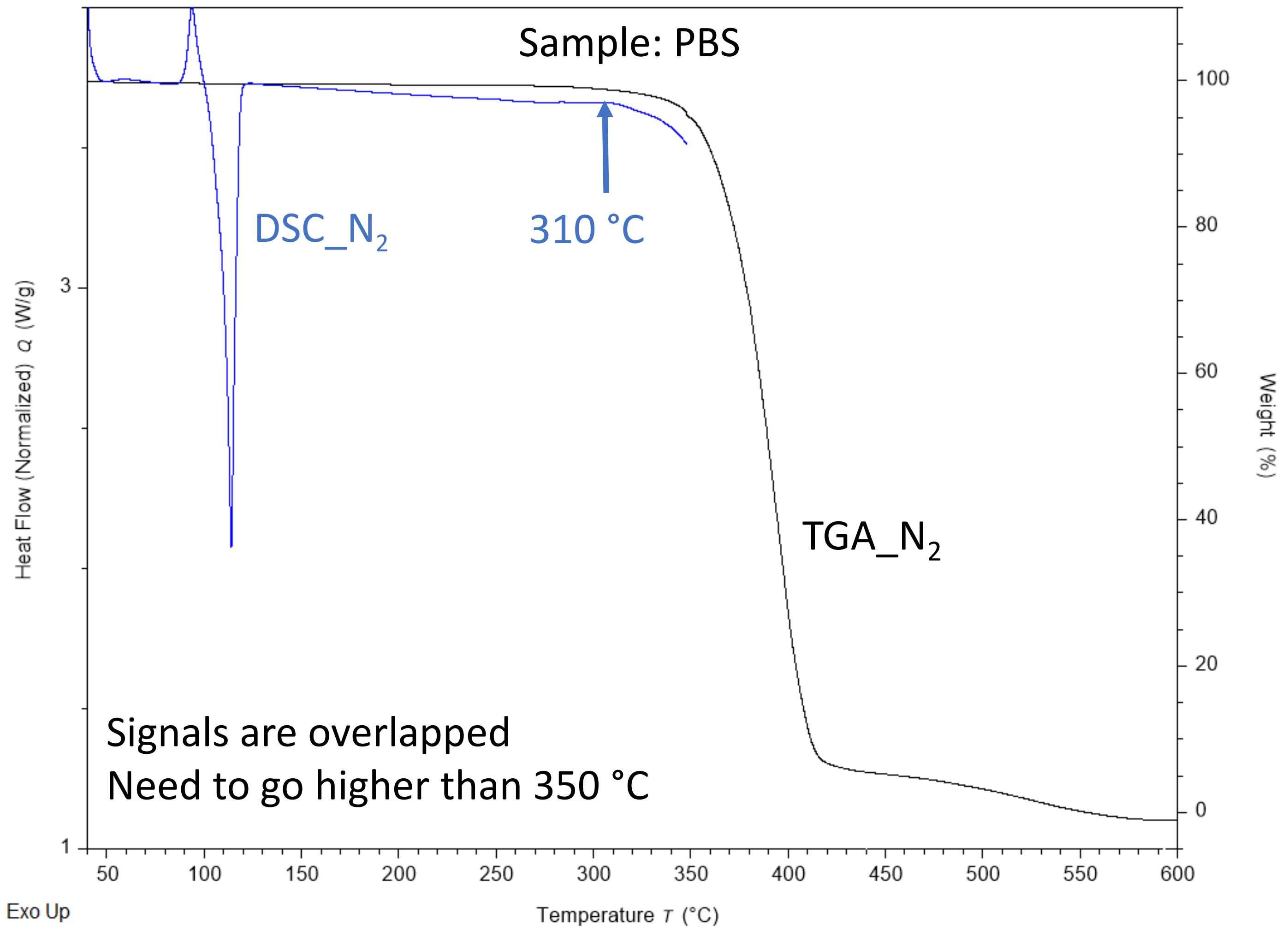
5 mg ± 0.5,
From 40 to 350 °C,
At 10 °C/min,



Under O_2: exo, fast
Under N_2: endo, slow

Exo phenomenon is really oxidation
Different mechanism under N_2 (endo)

Films analysis - Comparing DSC_N_2 vs TGA_N_2, 10°C/min



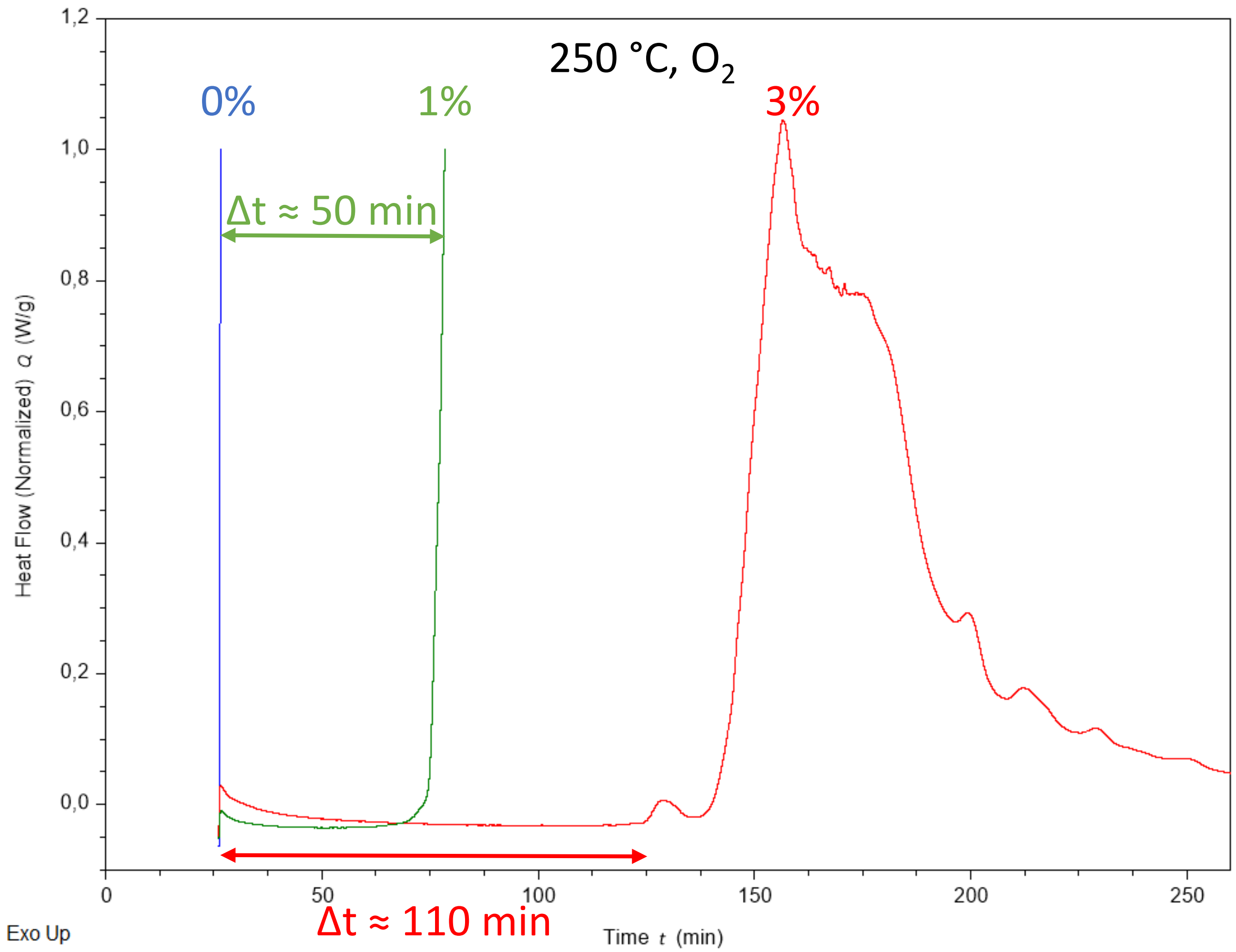
%Lignins	$T_{5\%loss}$ [°C] (TGA_N_2)	T_{onset} [°C] (DSC_N_2)
0%	350	310
1%	360	330
2%	361	340
3%	362	322

Endo phenomenon seems related to volatilisation

Films analysis - OIT

PBS
PBS + 1%Lignins
PBS + 3%Lignins

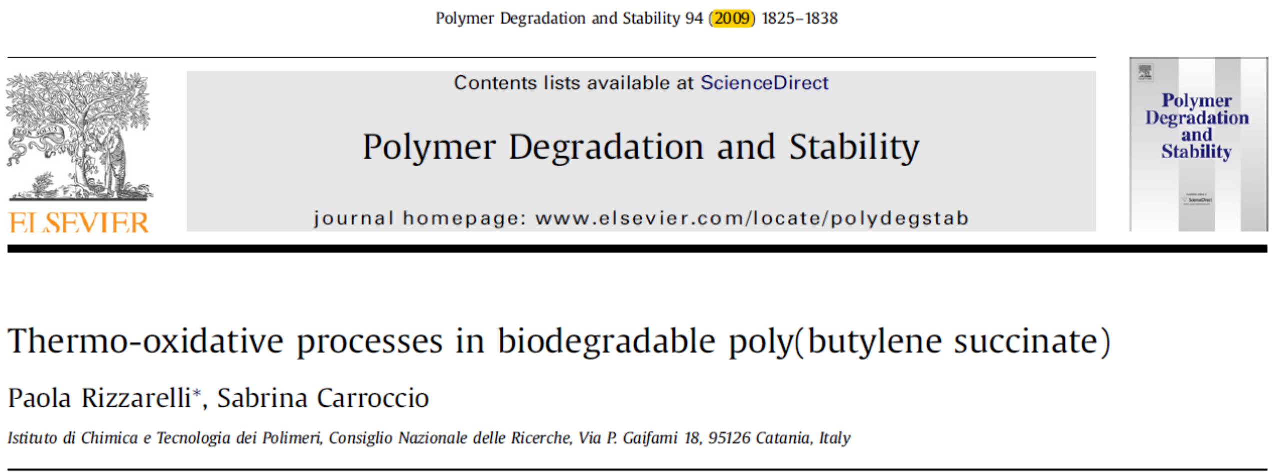
5 mg ± 0.5,
At 250 °C,
O_2 at 50 mL/min



Oxidation delayed by lignins at 250 °C
High effect of %Lignins

Degradation of PBS

Thermal ageing
- MALDI-TOF
- NMR
- SEC


Polymer Degradation and Stability 94 (2009) 1825–1838

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Thermo-oxidative processes in biodegradable poly(butylene succinate)

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1. Thermal oxidation

α-H abstraction
Hydroperoxyde intermediate

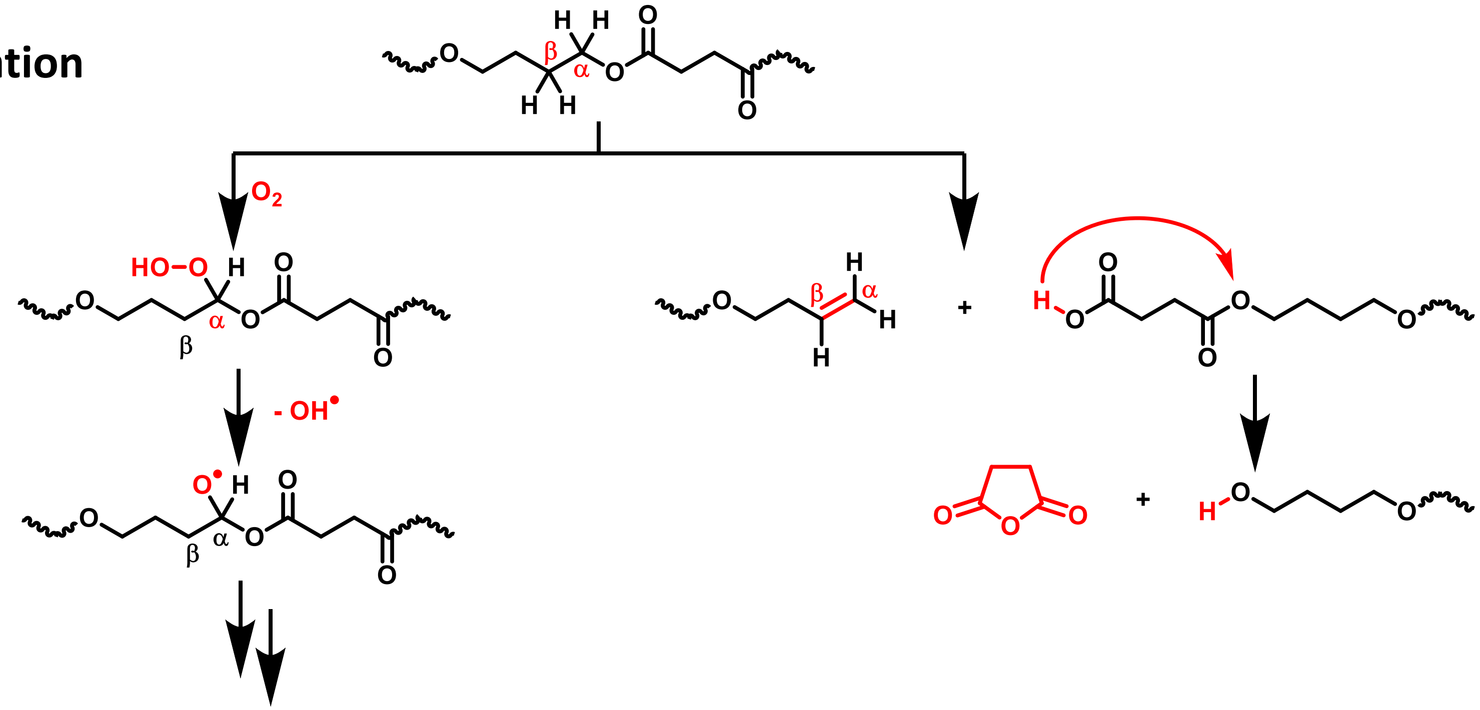
Hydroxy radical elimination

Radical rearrangement

2. Thermal degradation

β-H transfert
Bond scission

Release of succinic anhydride



Antiradical action of lignins
Misunderstood thermal stabilisation

Conclusions

- Lignins ↗ PBS stability
- Different degradation phenomena
  - If O_2 or N_2
  - If lignins or not

	Impact of	
	Lignins	%Lignins
TGA_N_2	↗	none
OOT_N_2	↗	weird
OOT_O_2	↗↗	↗
OIT_O_2	↗↗	↗↗

Kinetic effect? (OOT_O_2, OIT_O_2)

Effect of lignins towards O_2 > thermal

Thermal protection by lignins
Misunderstood mechanism under N_2

Analytical perspectives

- Slow down temperature gradient (TGA, OOT)
- « OIT »_N_2
- TGA_O_2
- Isothermal crystallisation

- XRD
- Rheological behavior
- Mechanical properties
  - Tensile tests
  - DMTA

Need methodology to understand stabilisation under N_2

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THANK YOU

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