RIT

Biochar as processing agent in PBAT

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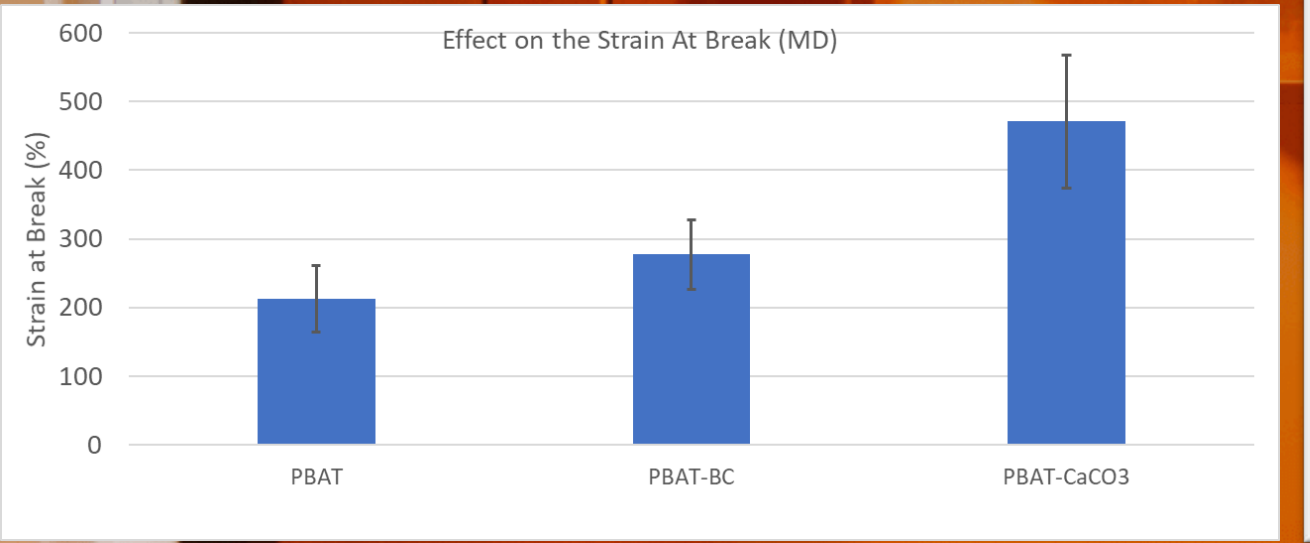
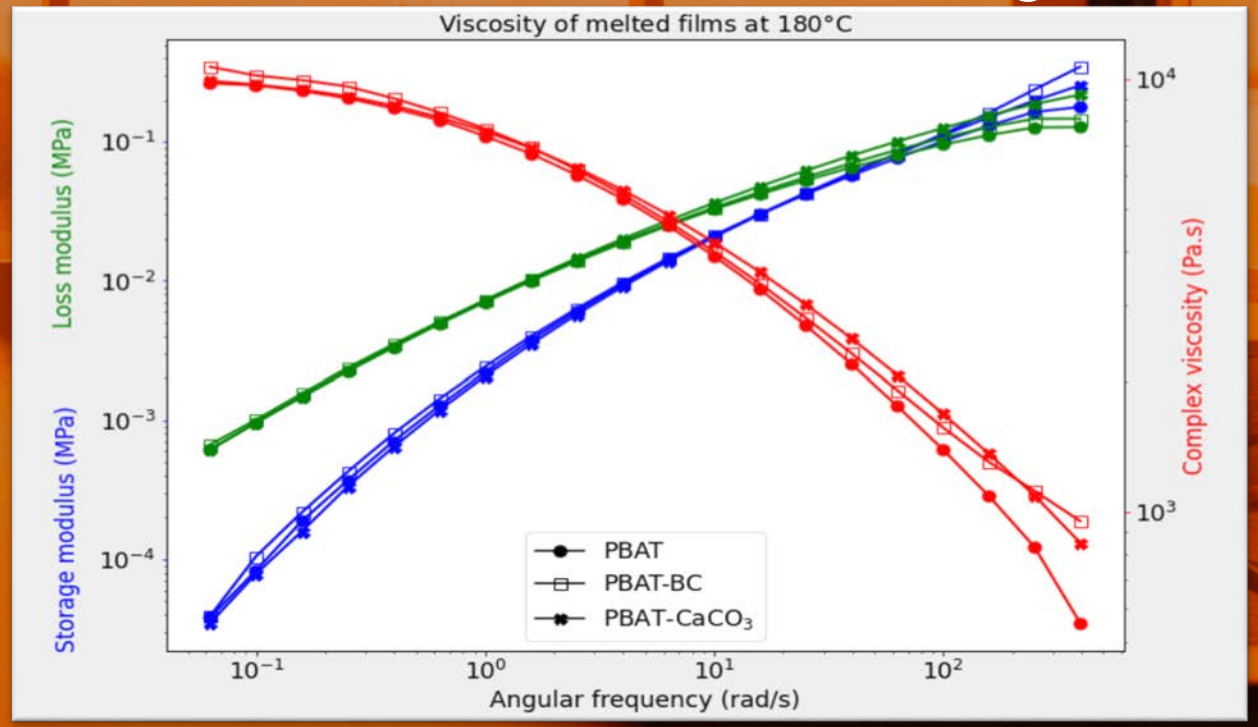




Biochar

Higher value applications enhances the economic viability of thermochemical conversion

- Product of thermochemical conversion of organic waste
- Agent of circular economy and carbon sequestration

(Draper K, 2015)

Why is this important?

Experiment design and samples

Biochar feedstocks

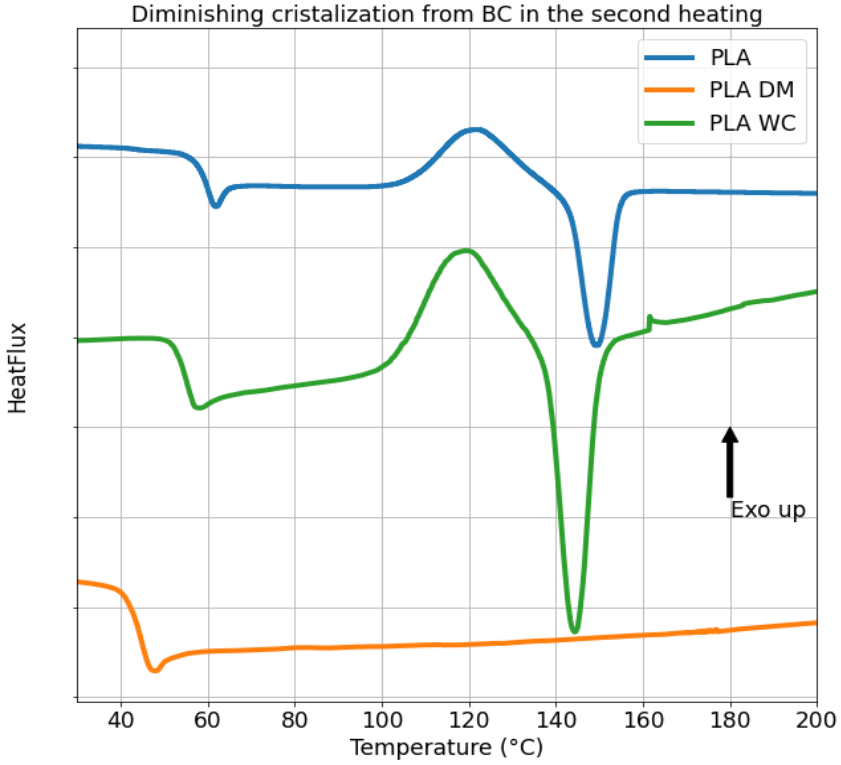
https://www.rit.edu/sustainabilityinstitute/blog/what-biochar-and-how-it-made

Results

Conclusions

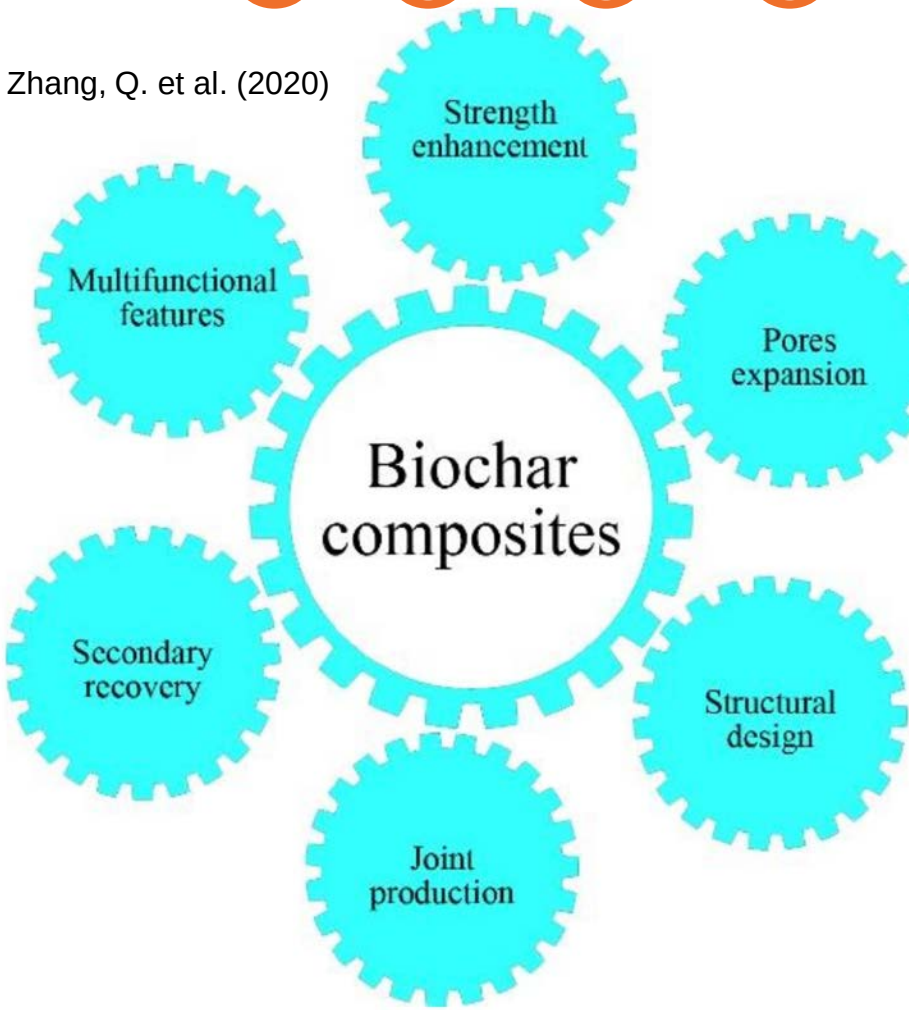
Biochar in plastics

- Feedstock affects effect of biochar in the composite
- Additive proportions effects are an unexplored area



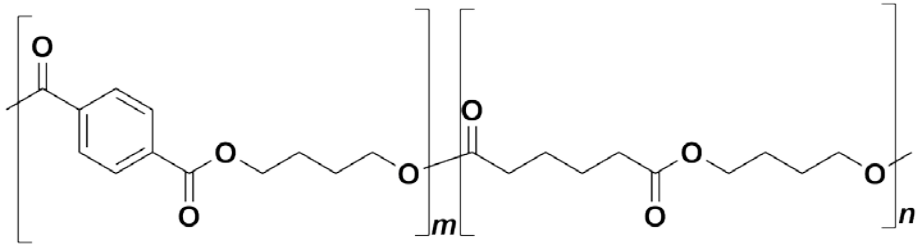
Hernandez-Charpak, Y et al. (2022)

Zhang, Q. et al. (2020)



What did we do?

Poly(butylene adipate-co-terephthalate) (PBAT)



PBAT Repeat unit
By DGH91 - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=31154046

Calcium Carbonate ($CaCO_3$)

Calcium Carbonate. Image from:https://fivestarchemicals.com/media/catalog/product/2/6/26-calcarb.png

- Anti-blocking
- Anti-slipping
- Widely used in industry
- **Extractive**
- Present in patents for agricultural films

Wood-based biochar (BC)

Powdered Biochar.
Image from https://ariescleantech.com/biochar/

- Affects surface
- Affects degradability
- Wood-based BC has a good adhesion to PBAT
- **Sustainable and renewable source**

Masterbatch process

PBAT 1:1

Brabender

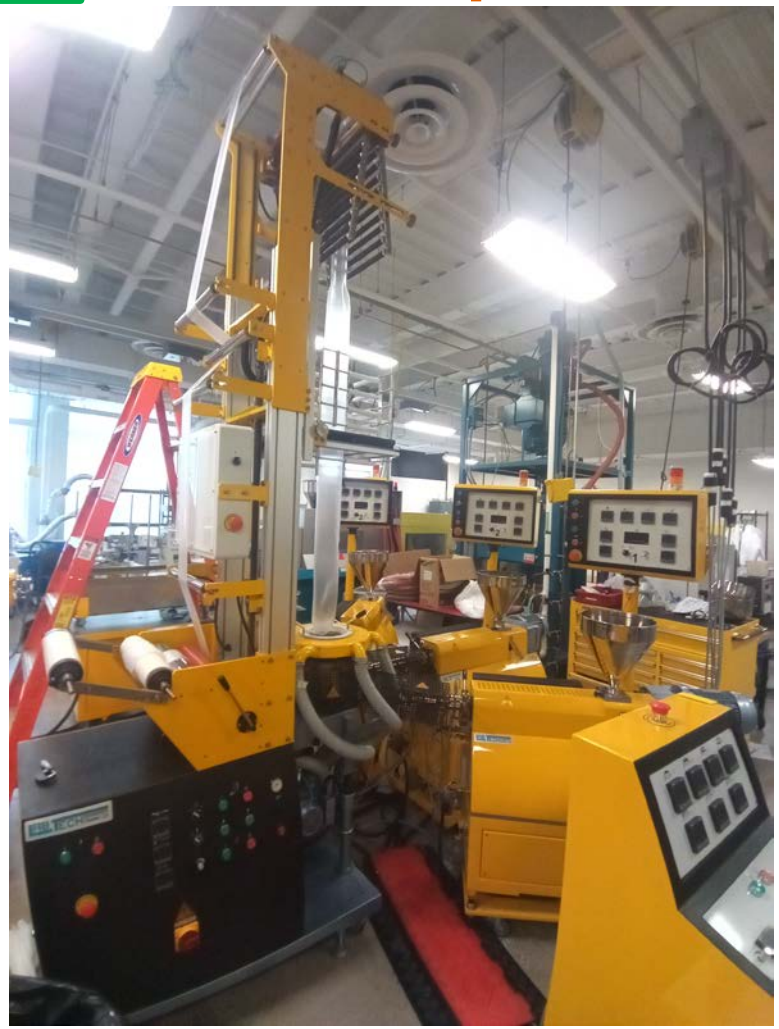
- Mixed for 5 min.
- 170 °C
- 60 rpm

Carver

- Pressed for 3 min at 180 °C
- Load 3 tons
- Cooled with water

PBAT 99:1

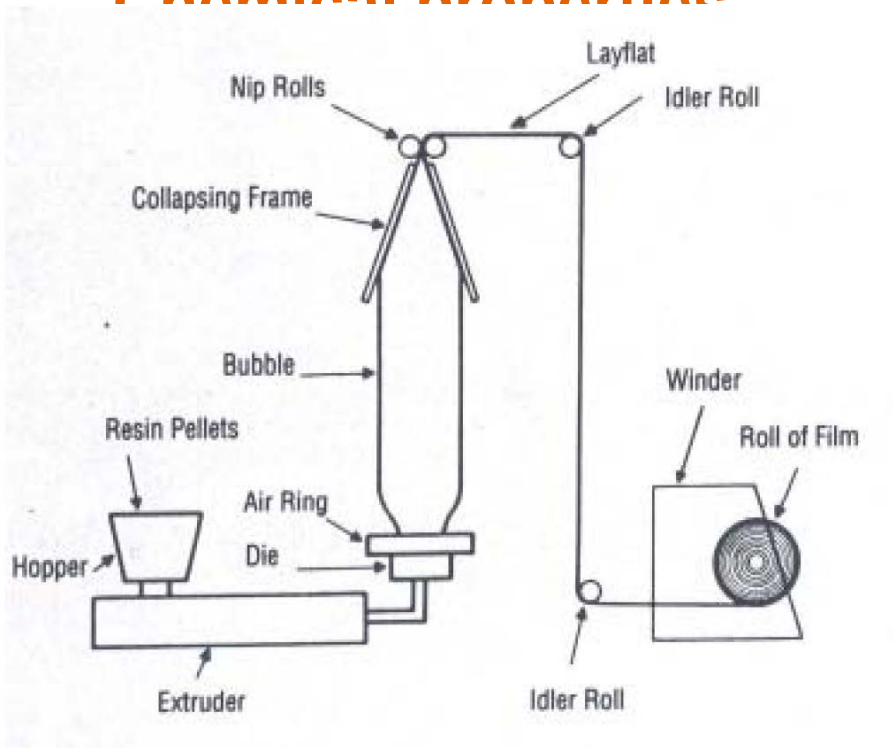
Filmblown process



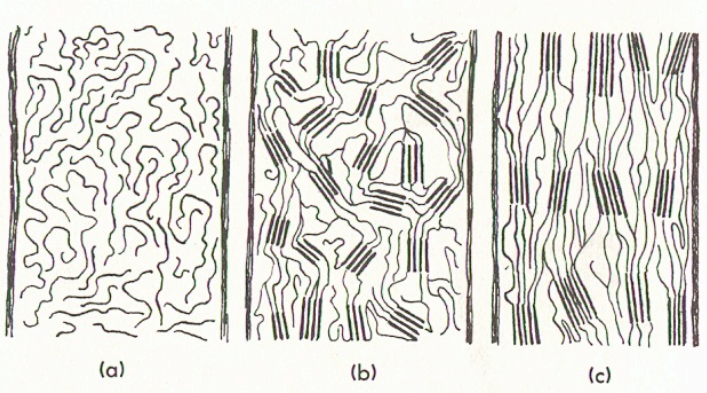
Lab-tech three layer blown film line 250mm wide with 12.5mm extruders

Manufacturing

Chemical properties



(Lyondellbasel,2009)

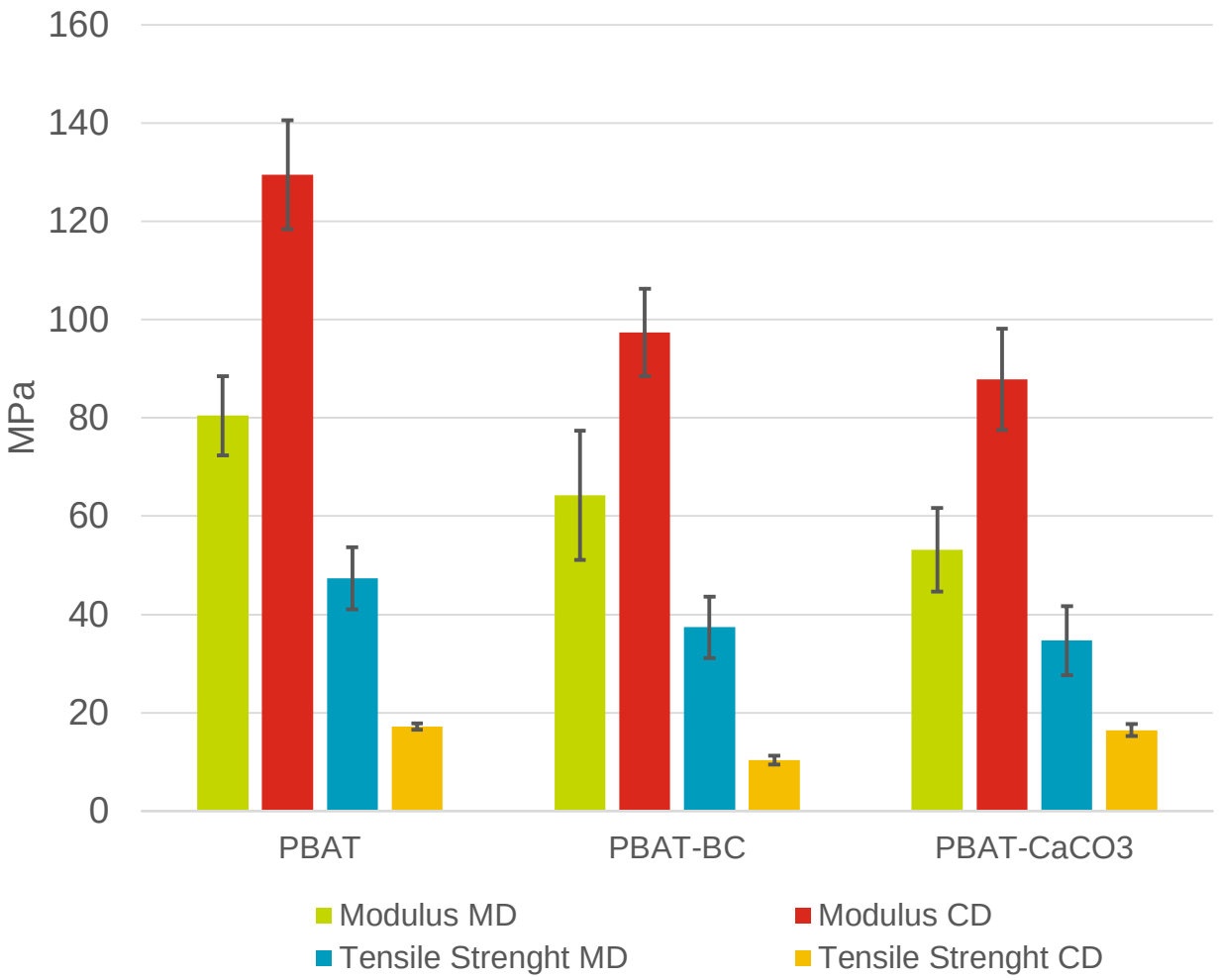


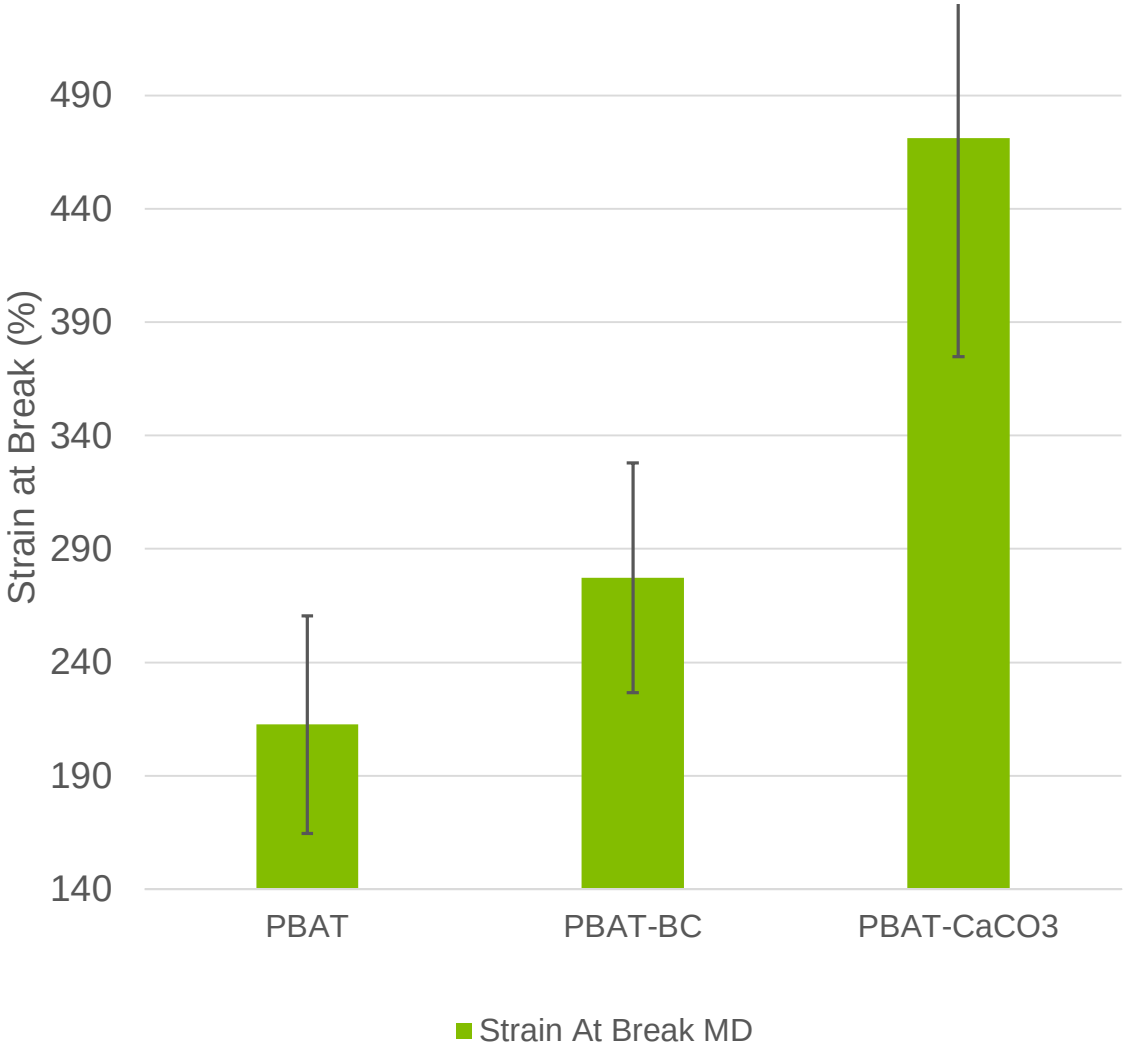
Morphology

- Scanning electron microscopy (SEM)

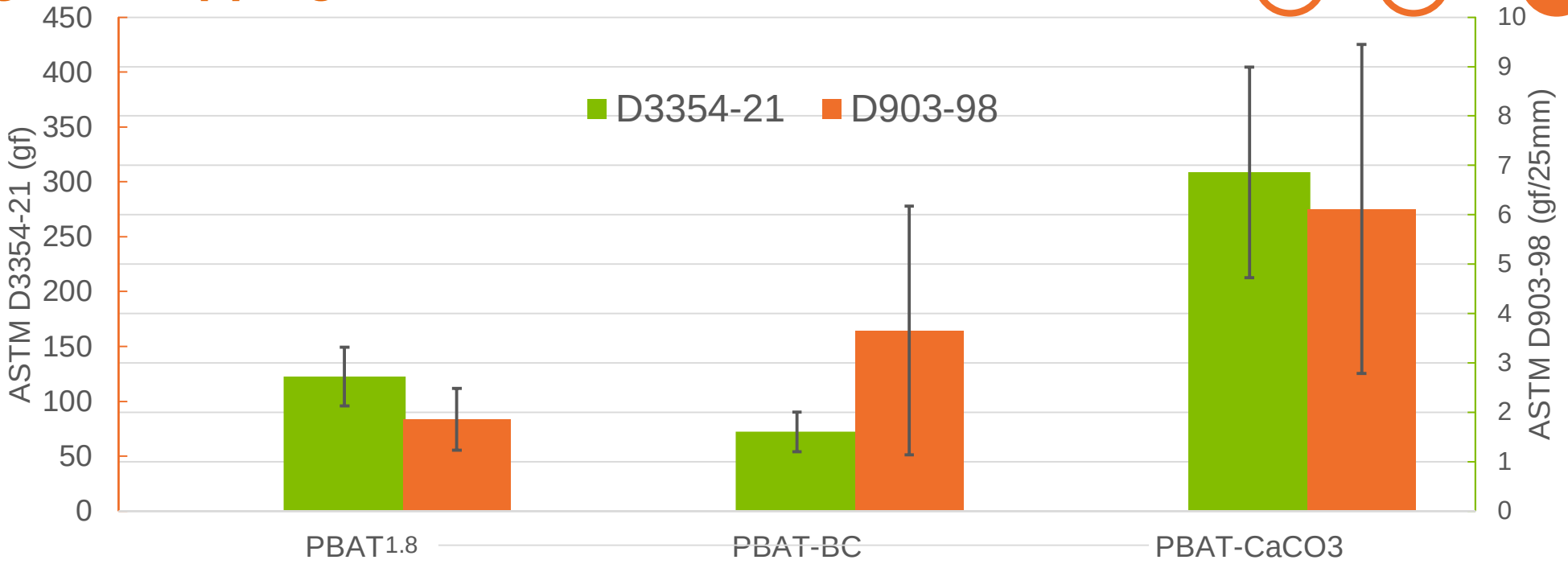
Mechanical properties

Lower modulus and higher strain at break (usually is the inverse when filling a polymeric matrix)

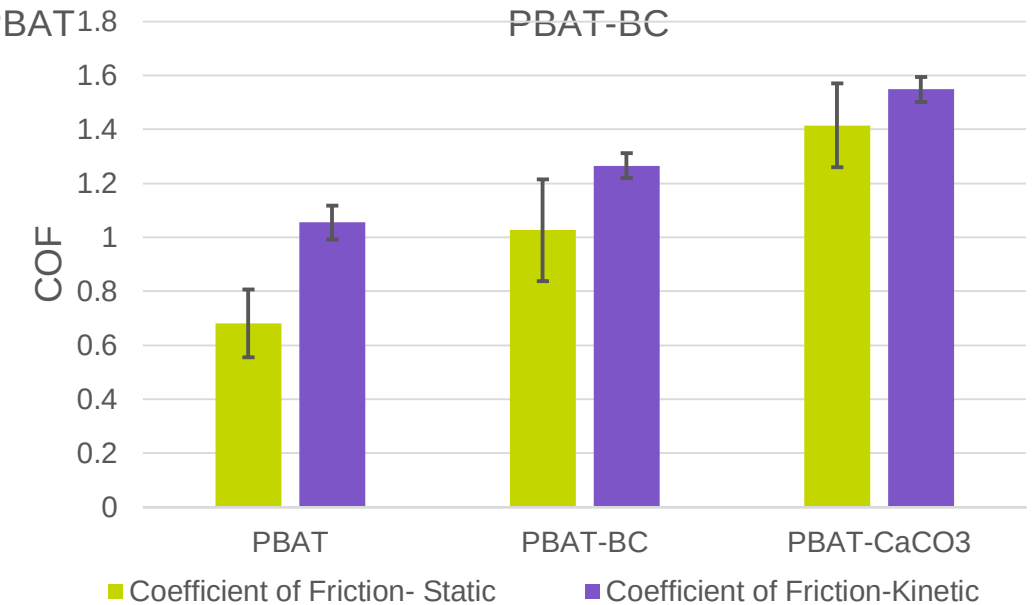




Blocking and slipping

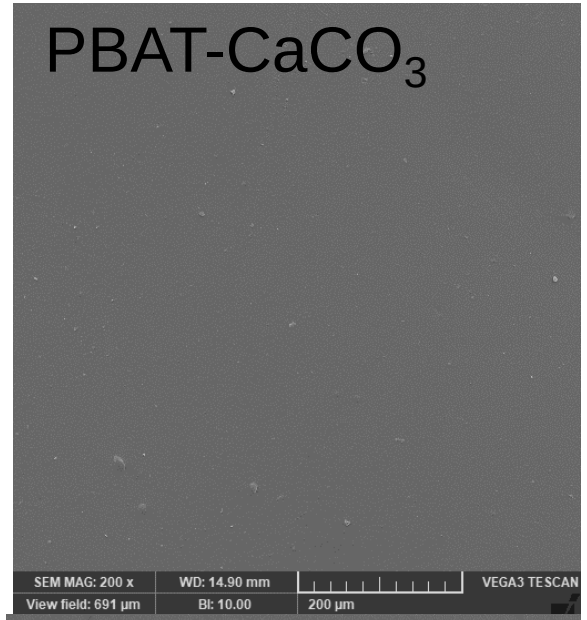


ASTM D3354, is on the whole film and reports maximum force

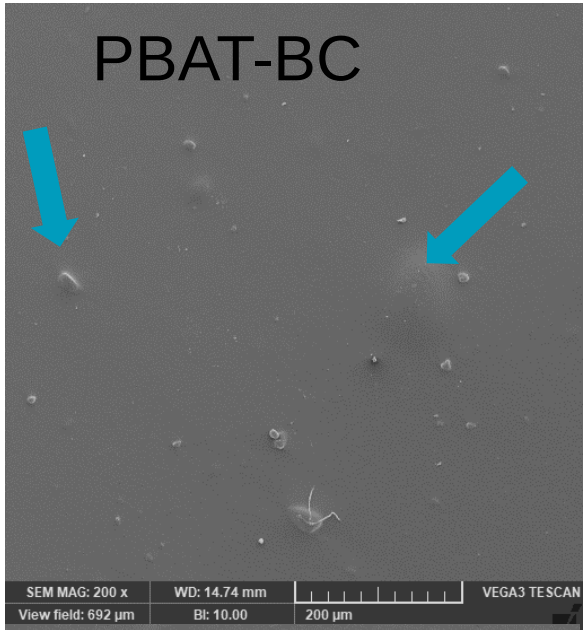


ASTM D903, is on a set width and reports an average force

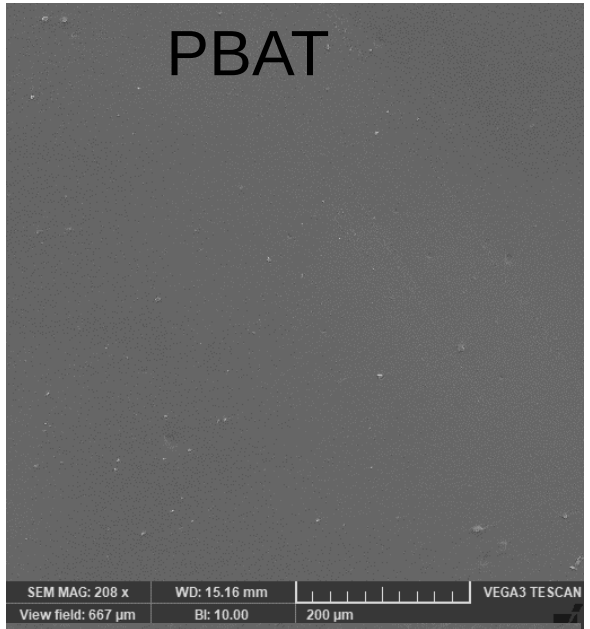
Morphology

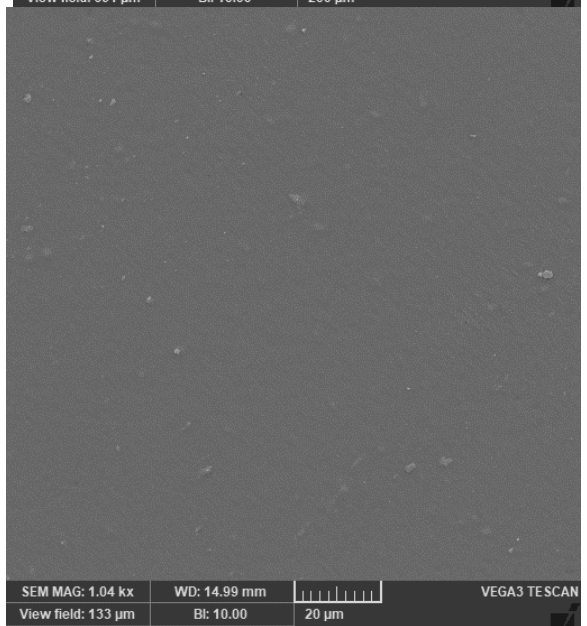


200 x

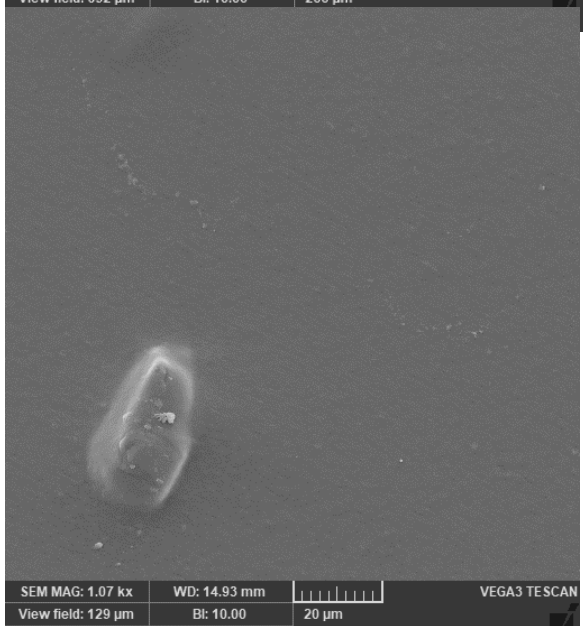


200 x

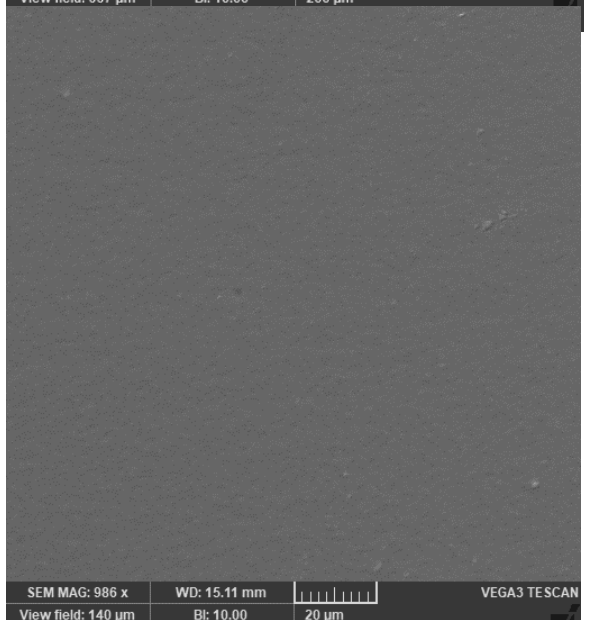




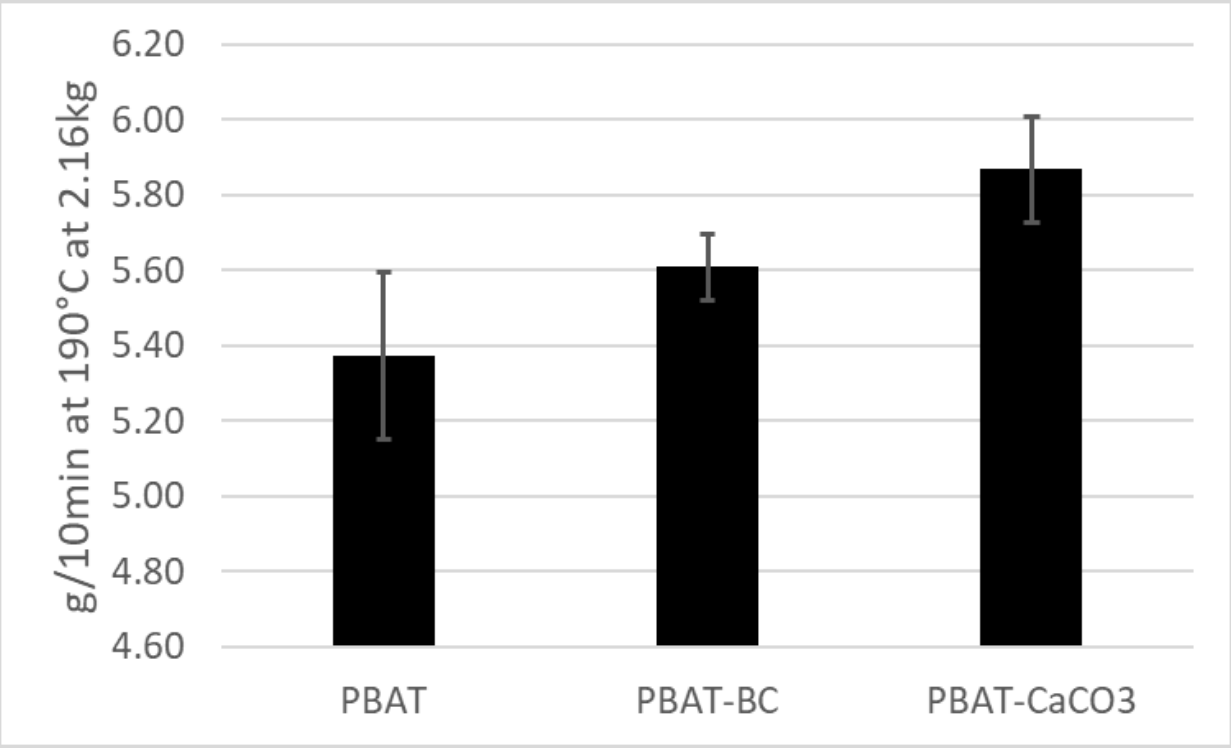
1000 x

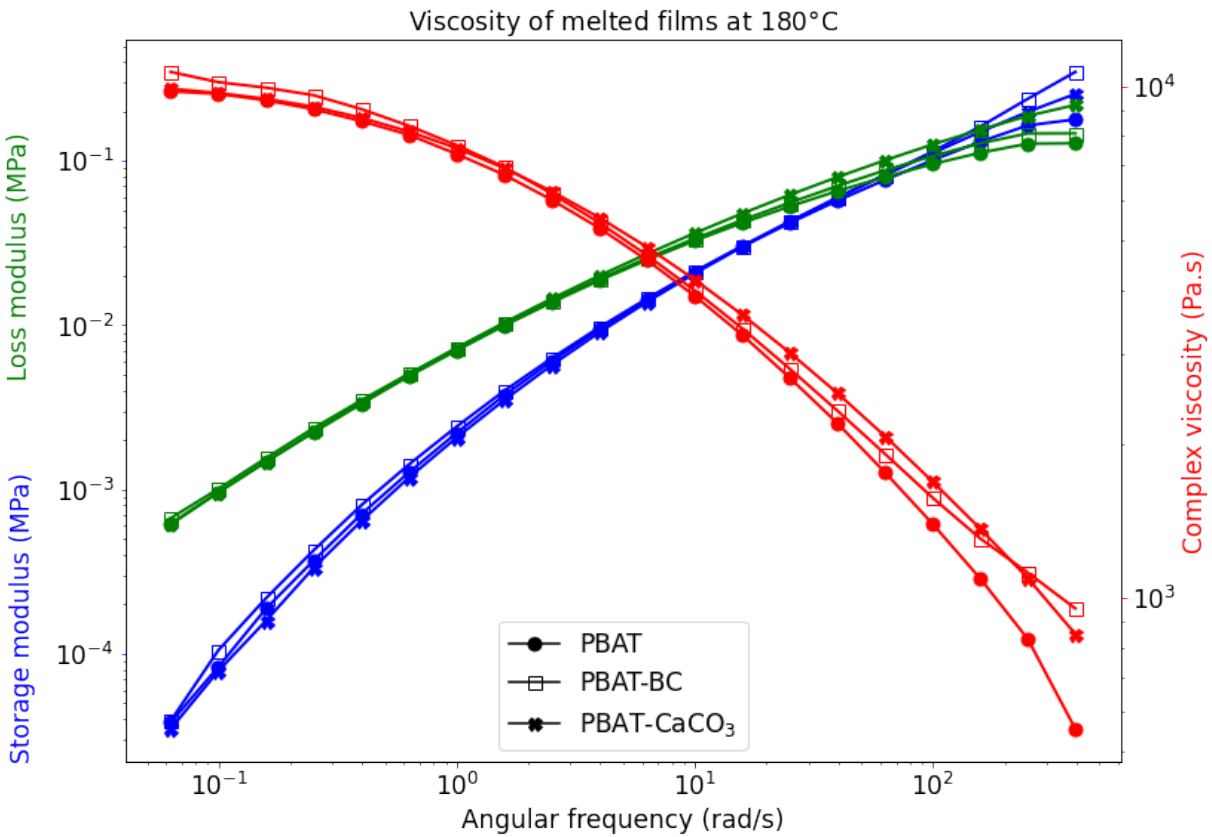


1000 x



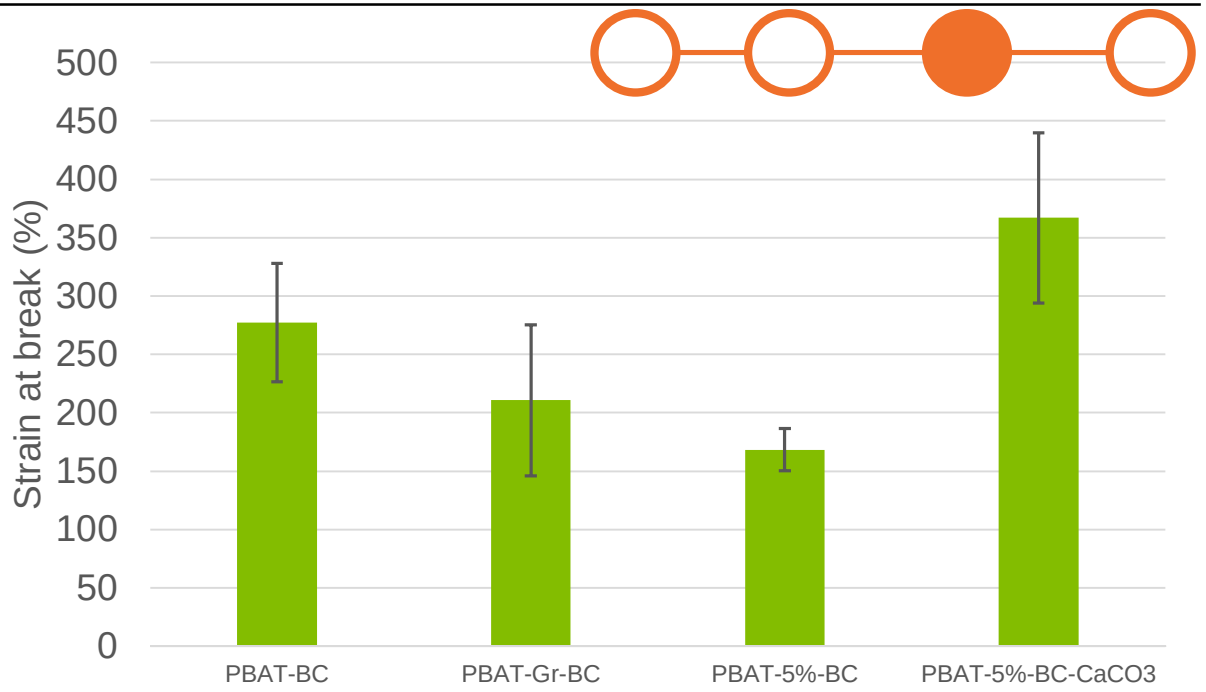
Rheological properties



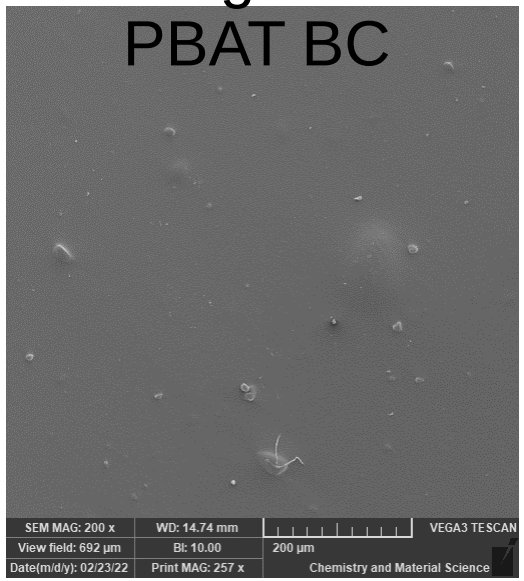


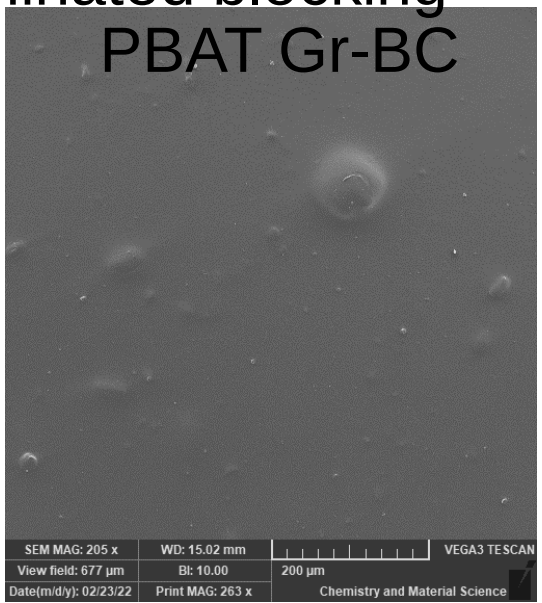
- Both increased MFI without affecting viscosity
- Additional secondary forces leading to higher blocking and friction

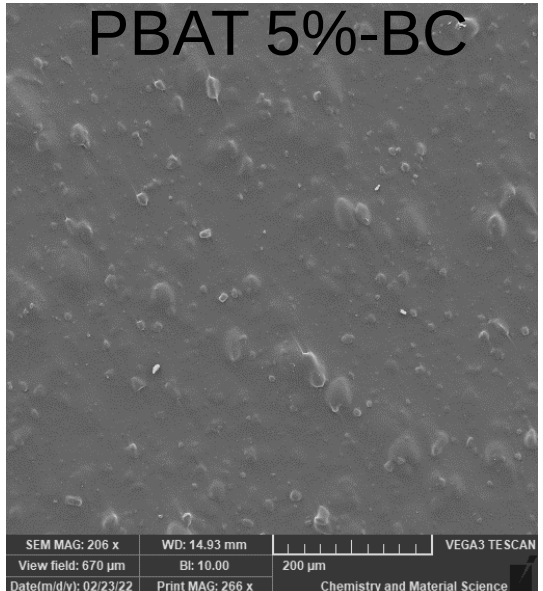
Additional formulations

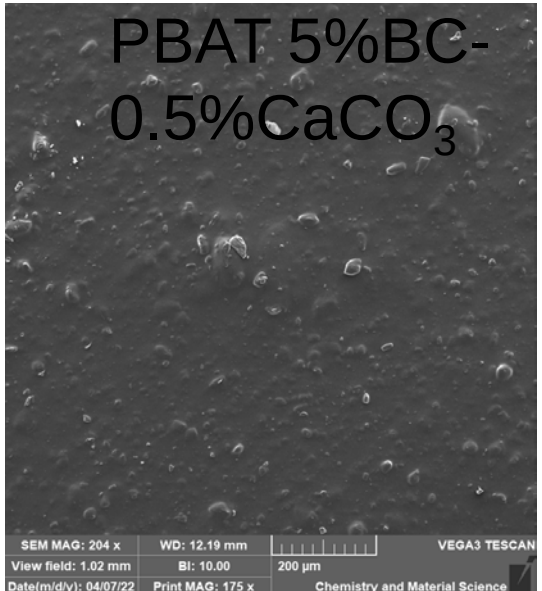


- Additional loading did not show increased elongation but eliminated blocking



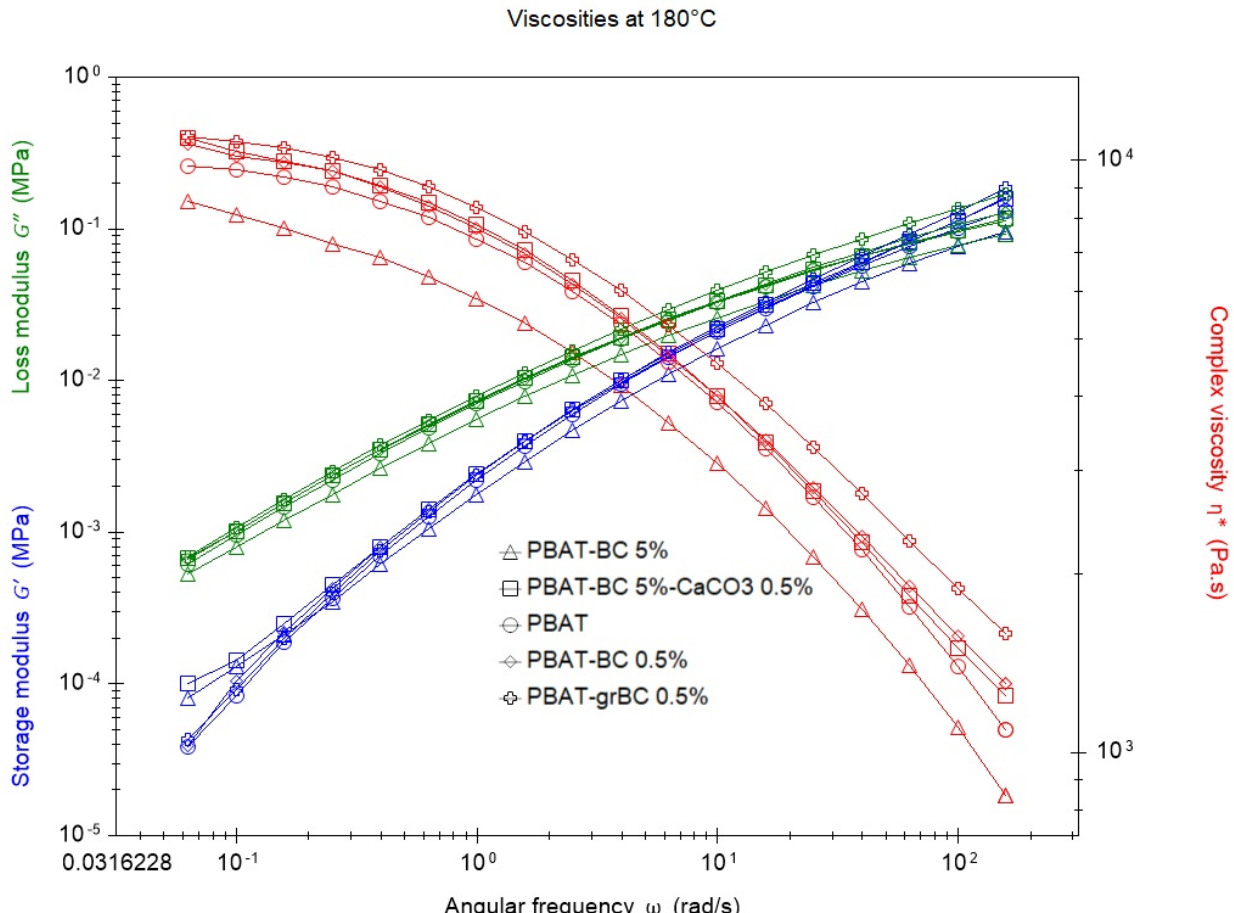


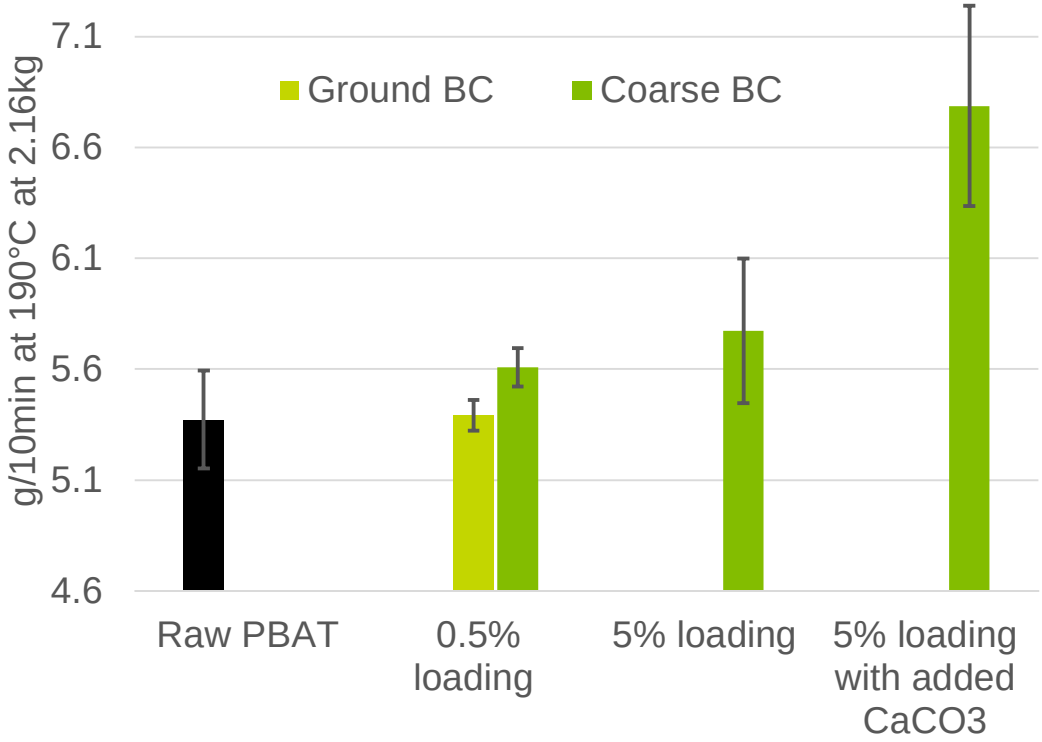




Additional experimentation

- MFI shows a different flow from the finer BC. Initial particle size affects the interaction.





- Viscosity did not increase with higher loading

Conclusions

Wood-based biochar (BC)

$CaCO_3$ in additive proportion within PBAT

- BC increased the strain at break, less than $CaCO_3$.
- BC barely affected processing properties, $CaCO_3$ had a significant impact on them.
- Neither BC nor $CaCO_3$ affected viscosity but increased the MFI of the PBAT.

BC, when added as an additive in PBAT, increased flow and elongation without affecting processing. Future research should be made to assess it's potential for injection molding or other shape filling extrusions applications.

Next steps

- Explore the effects of BC on traditional, high-volume polymers (LDPE).
- Additional experimentation to pinpoint the mechanisms that lead additional interactions in the $CaCO_3$

References!

Thank you!

FOUNDATION FOR FOOD & AGRICULTURE RESEARCH

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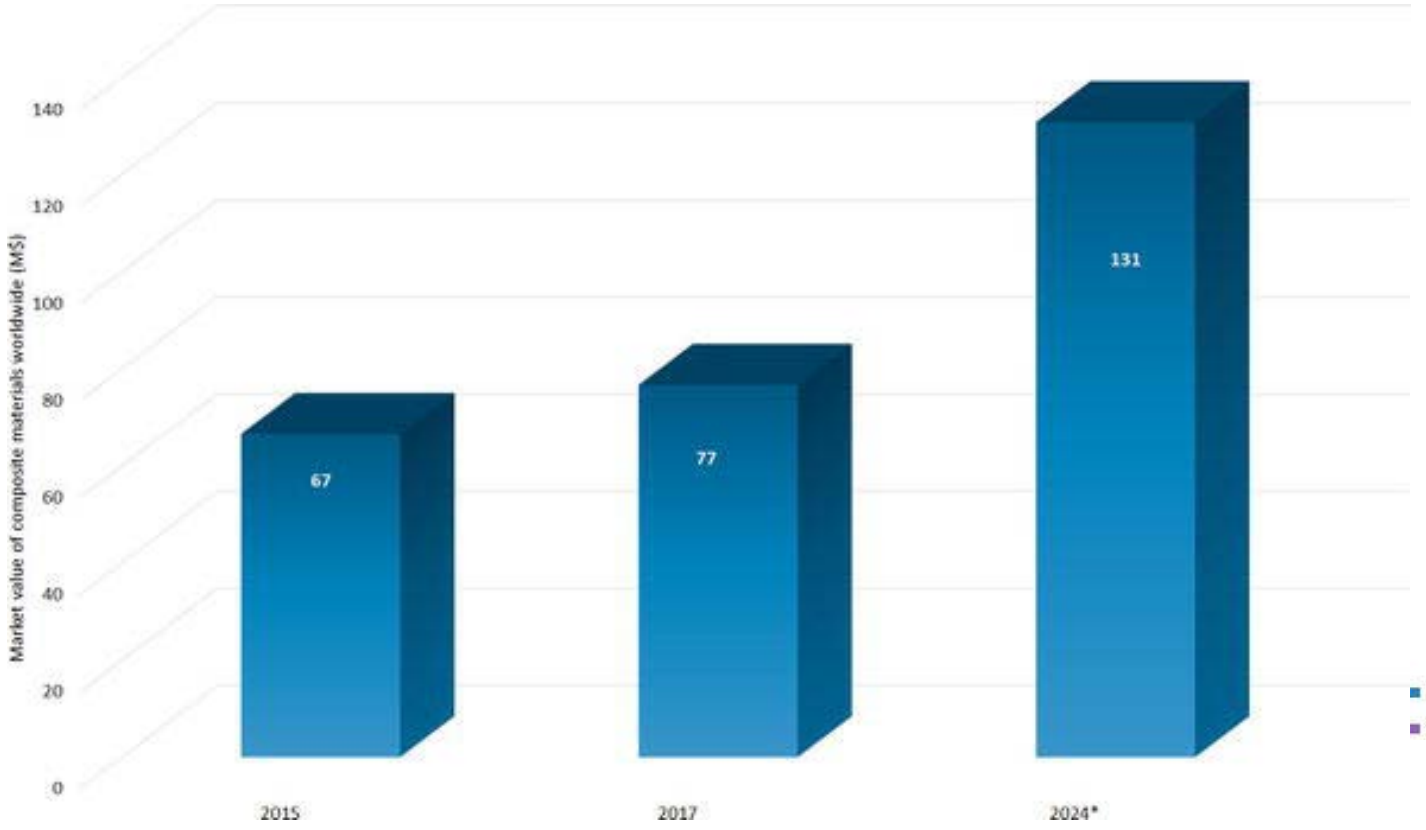
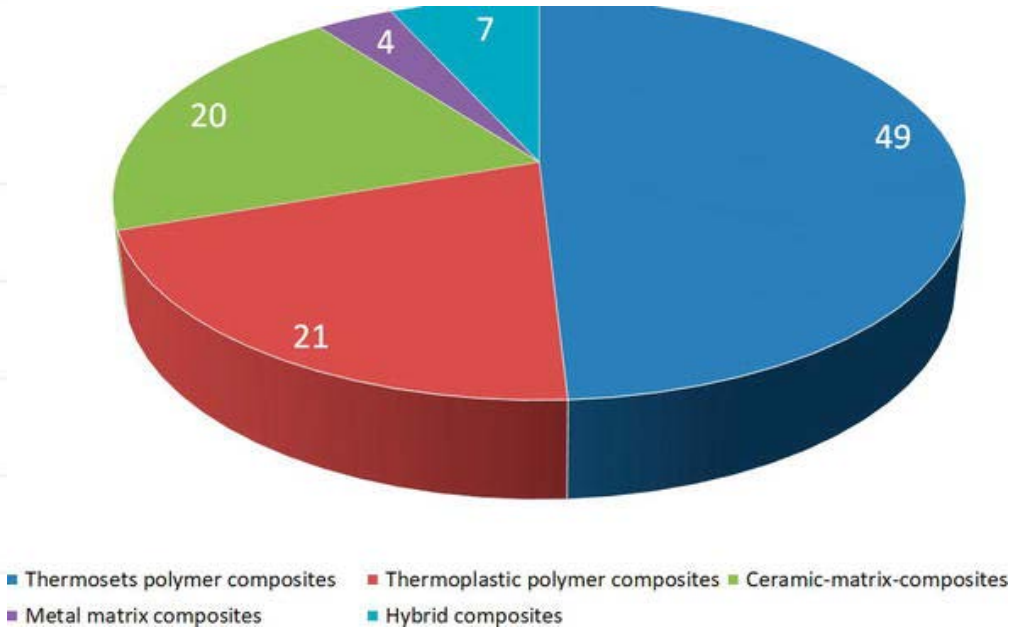
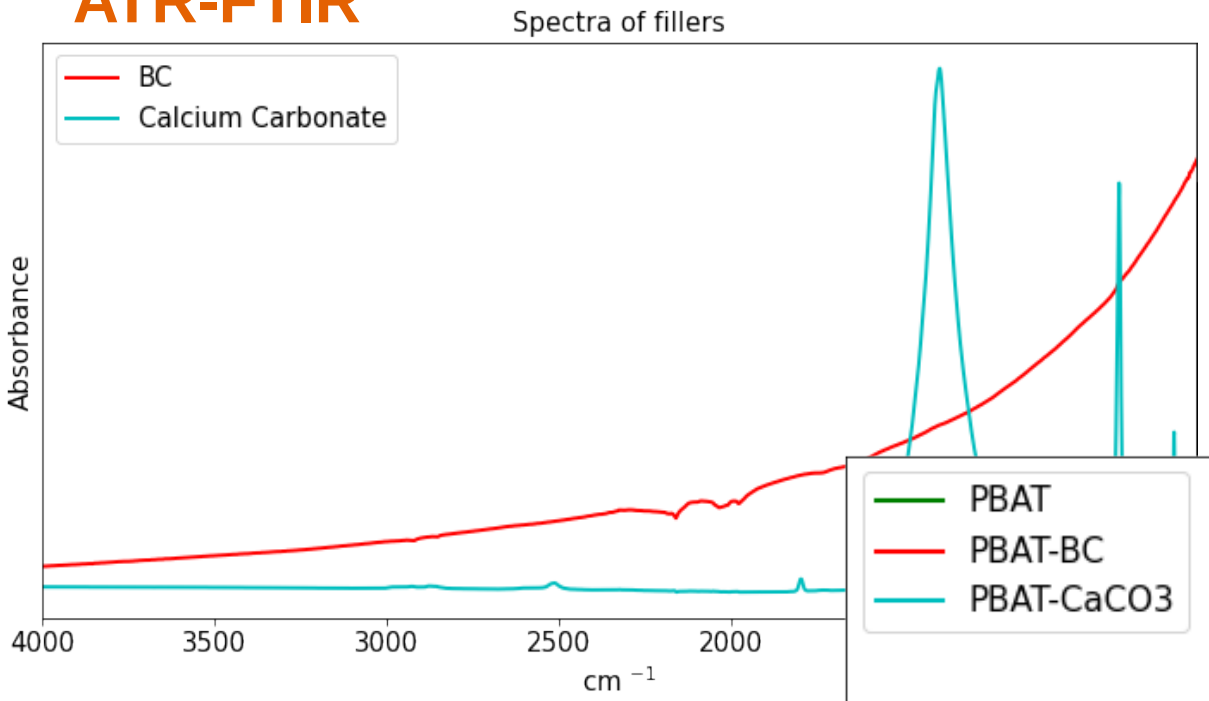


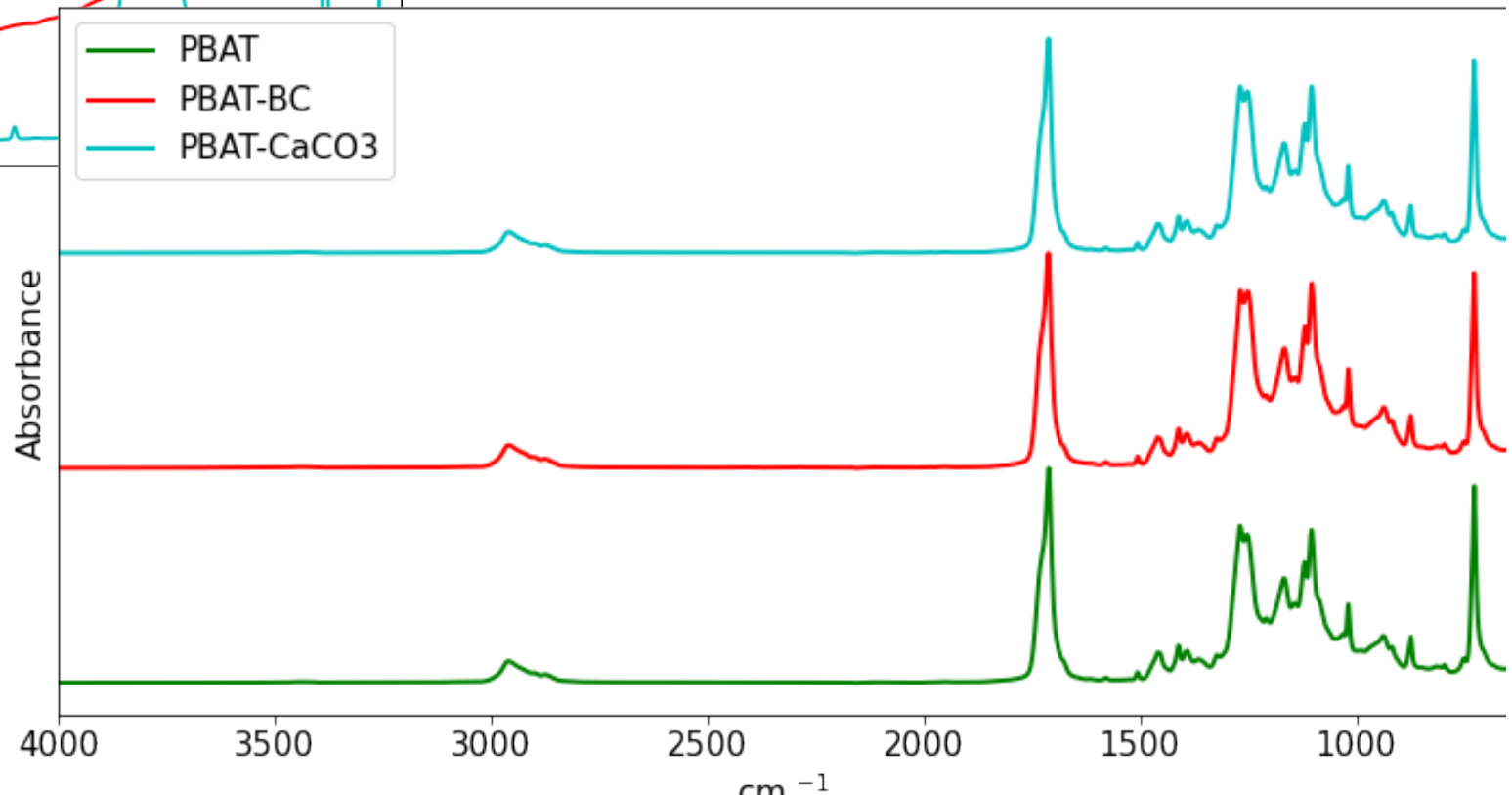


(Bartoli, 2020)

ATR-FTIR



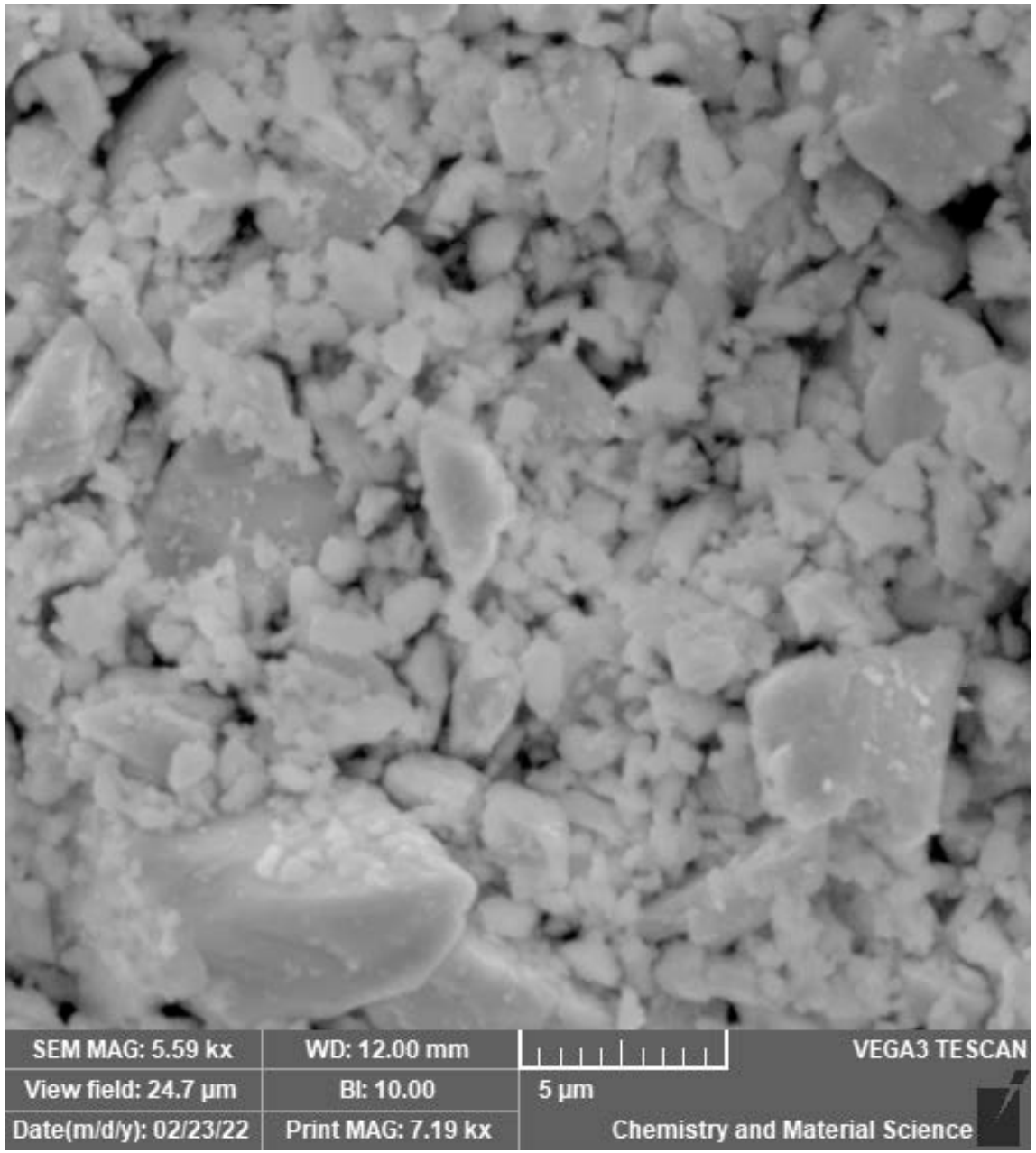
No differences on the blends despite the strong difference of the additives

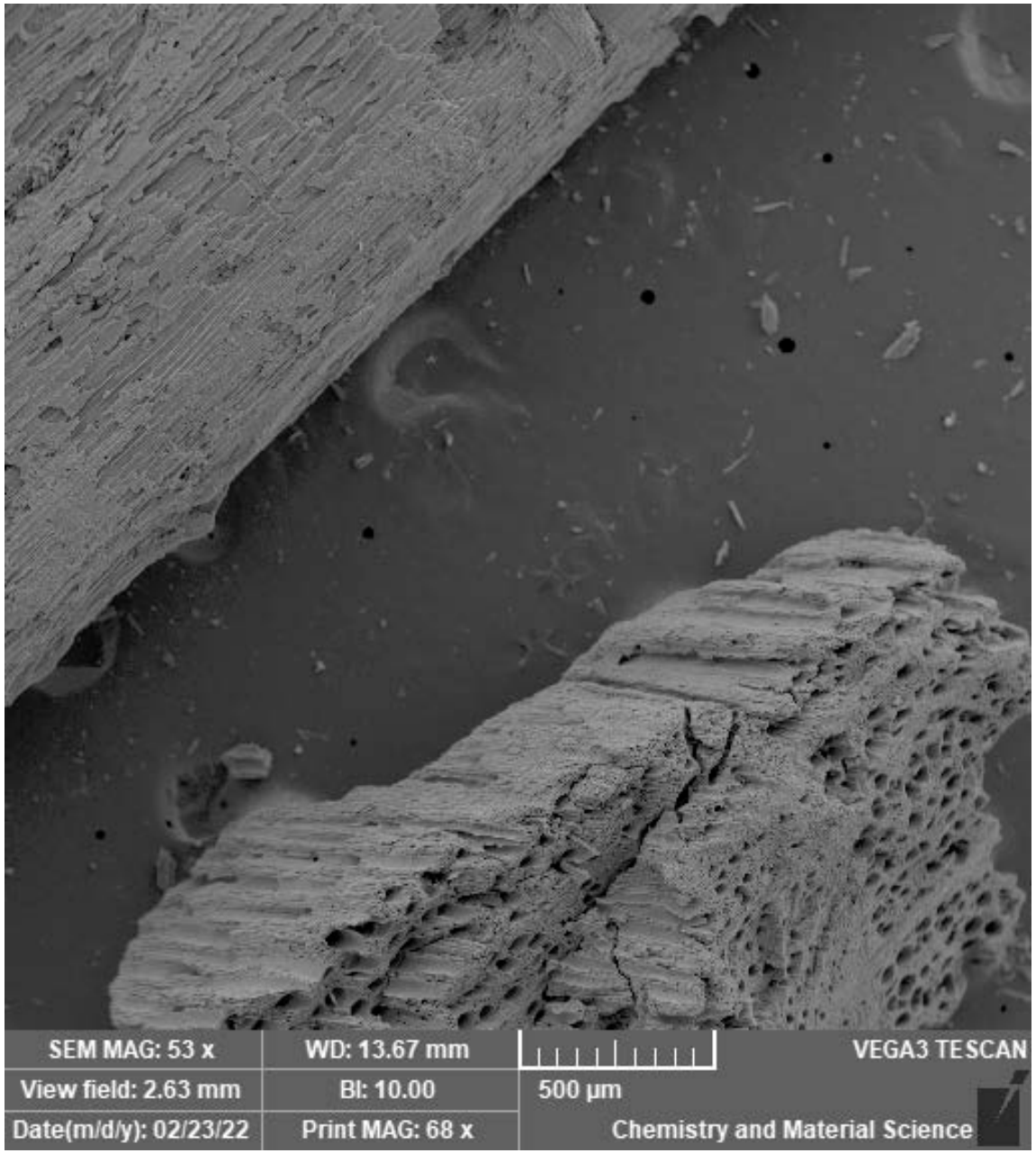


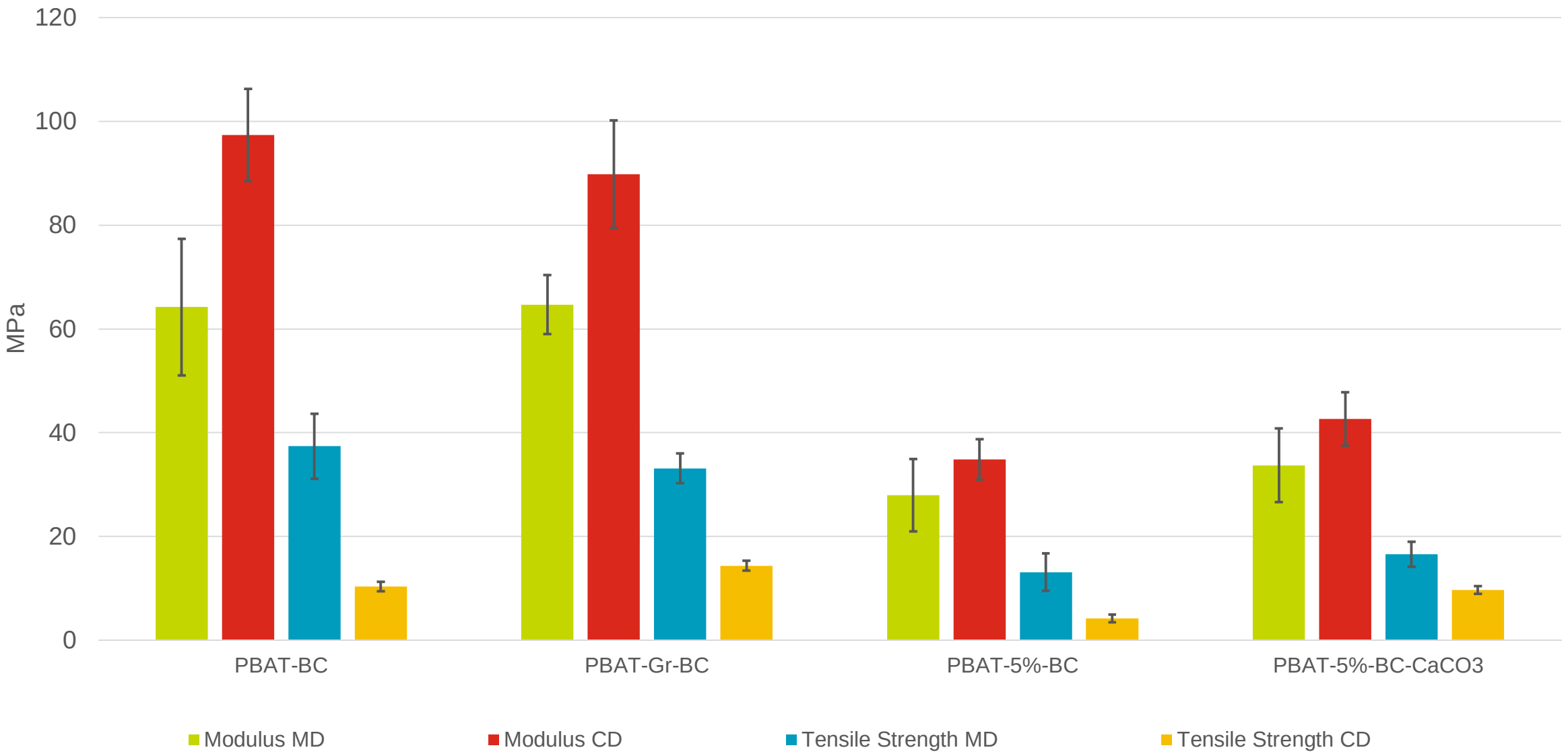
Thermal properties

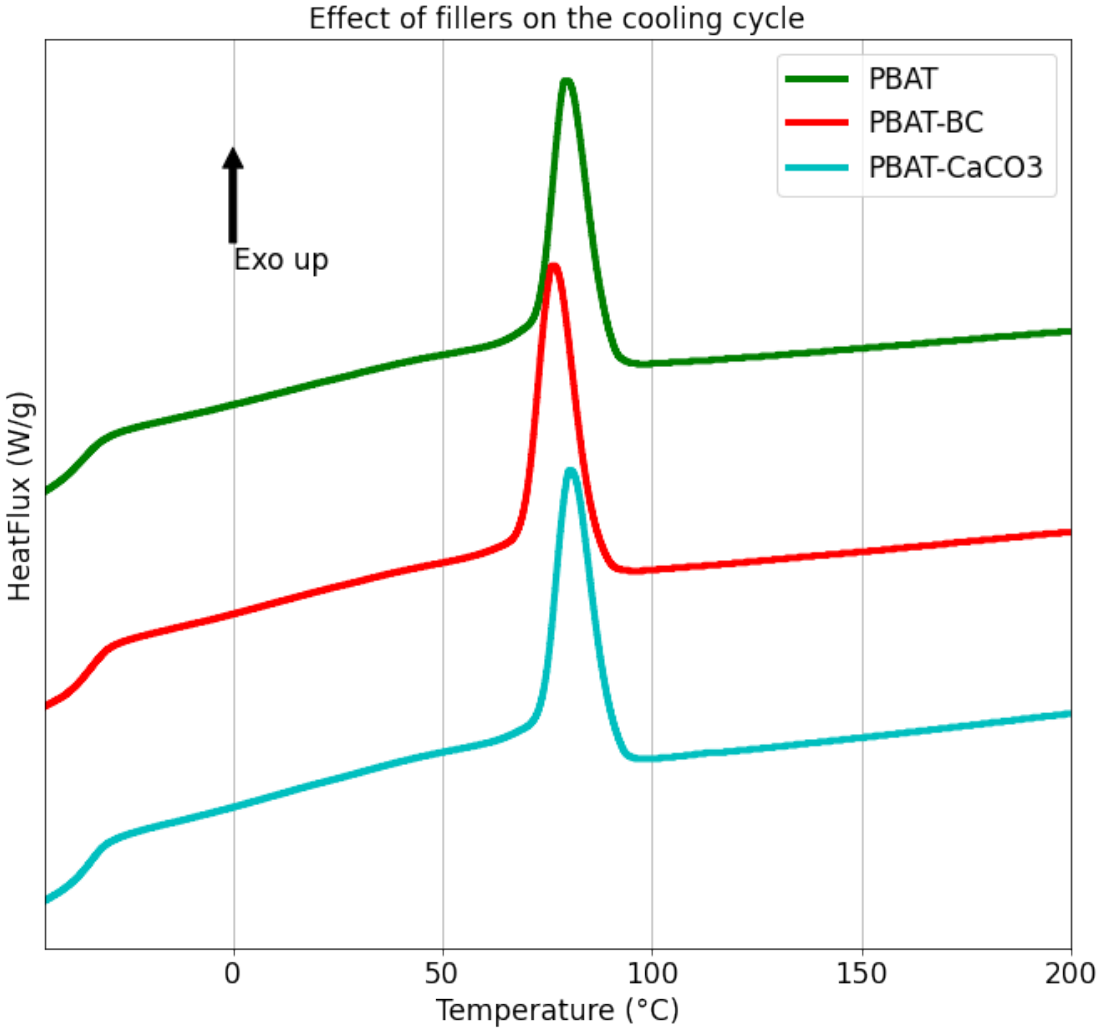
Second heat BC sample is more crystalline, and crystallization occurs at a lower temperature. But when the loading increases, little difference is seen.

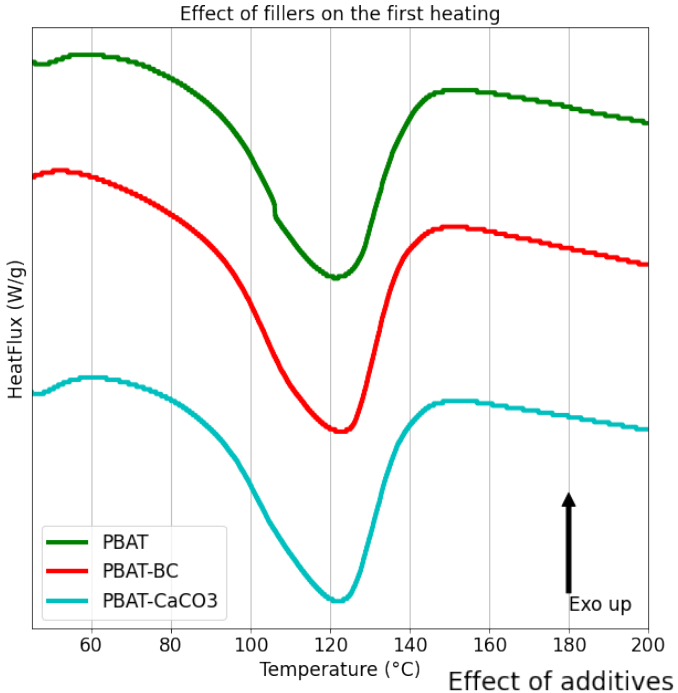
	DSC-1st Heat	DSC-2nd Heat	DSC-Cooling	TGA
	χ_c(%)	χ_c(%)	T_c (°C)	T_{offset} (°C)
PBAT	11.3 ± 0.7[a]	8.8 ± 0.2[b]	78.6 ± 1.4[b]	367.2 ± 1.2[a]
PBAT BC 0.5%	12.2 ± 0.5[a]	9.5 ± 0.1[a]	76.3 ± 0.2[a]	368.0 ± 2.0[a]
PBAT CaCO3	11.7 ± 0.3[a]	8.7 ± 0.1[b]	79.3 ± 1.4[b]	369.1 ± 2.7[a]
PBAT Gr-BC 0.5%	11.5 ± 1.0[a]	9.0 ± 0.7[ab]	77.8 ± 1.4[a]	369.6 ± 1.1[a]
PBAT BC 5%	11.8 ± 0.1[a]	8.3 ± 0.4[b]	81.6 ± 0.3[b]	367.8 ± 2.8[a]
PBAT BC 5% $CaCO_3$	11.8 ± 0.1[a]	8.4 ± 0.1[b]	81.8 ± 0.3[b]	367.6 ± 2.7[a]

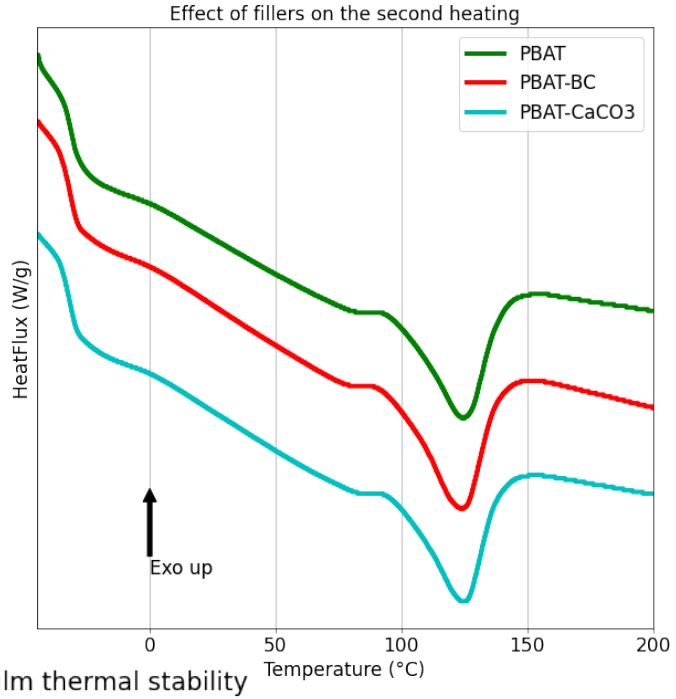

SEM MAG: 5.59 kx
WD: 12.00 mm
VEGA3 TESCAN
View field: 24.7 µm
BI: 10.00
5 µm
Date(m/d/y): 02/23/22
Print MAG: 7.19 kx
Chemistry and Material Science

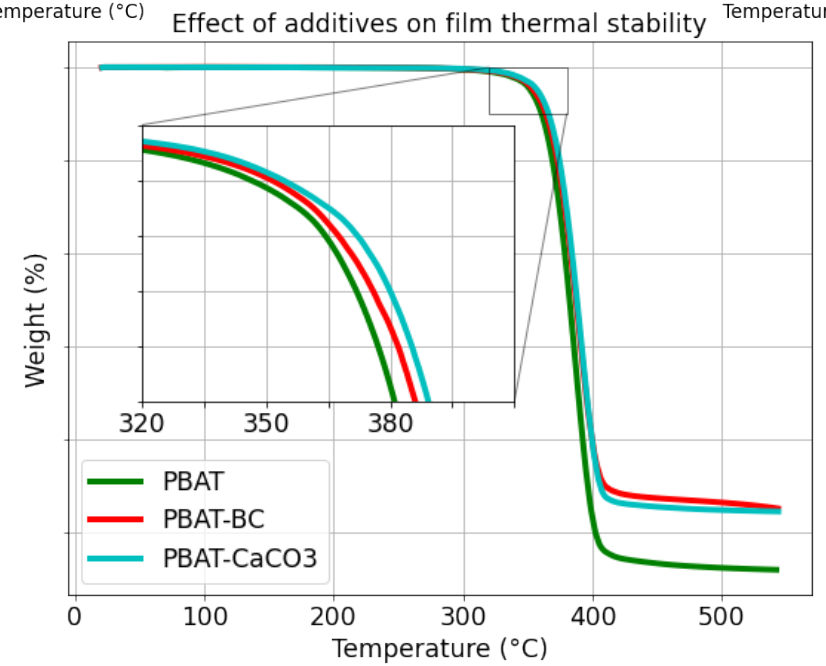

SEM MAG: 53 x
WD: 13.67 mm
VEGA3 TESCAN
View field: 2.63 mm
BI: 10.00
500 µm
Date(m/d/y): 02/23/22
Print MAG: 68 x
Chemistry and Material Science

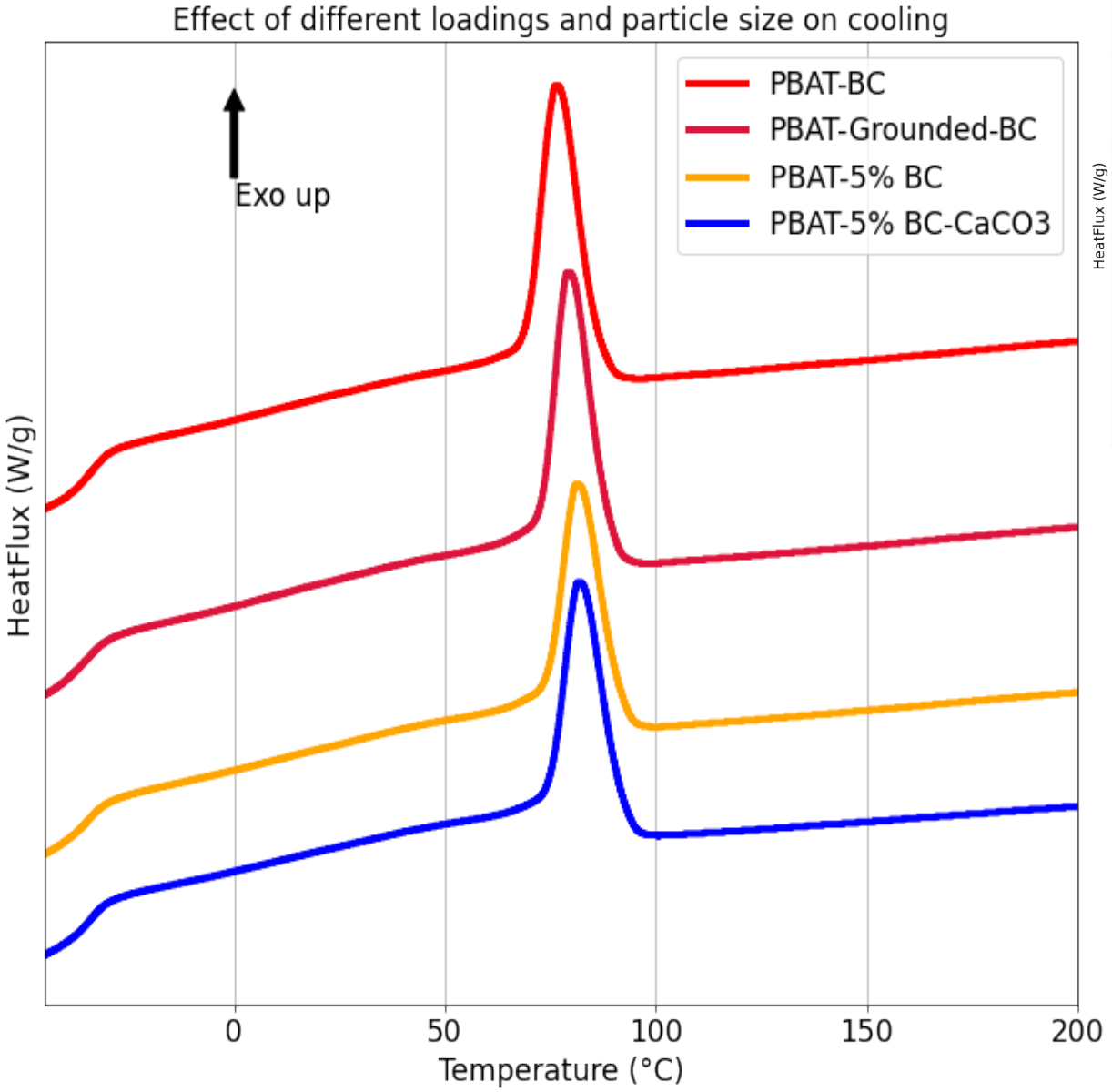

120
100
80
60
40
20
0
MPa
PBAT-BC
PBAT-Gr-BC
PBAT-5%-BC
PBAT-5%-BC-CaCO3
Modulus MD
Modulus CD
Tensile Strength MD
Tensile Strength CD

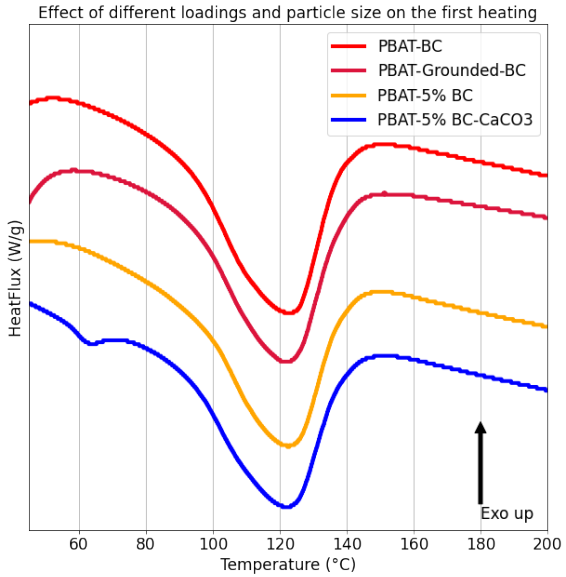

Effect of fillers on the cooling cycle
PBAT
PBAT-BC
PBAT-CaCO3
Exo up
HeatFlux (W/g)
0
50
100
150
200
Temperature (°C)

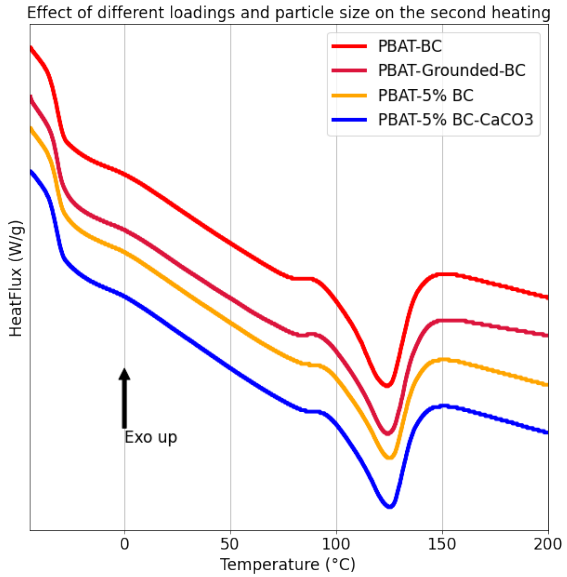

Effect of fillers on the first heating
HeatFlux (W/g)
PBAT
PBAT-BC
PBAT-CaCO3
Exo up
60
80
100
120
140
160
180
200
Temperature (°C)

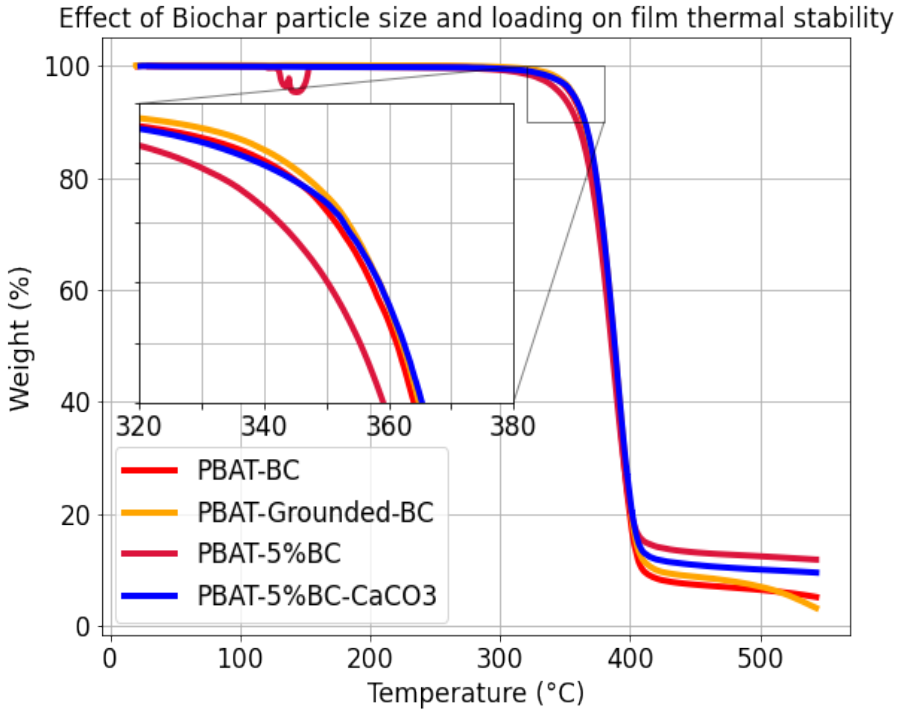

Effect of fillers on the second heating
PBAT
PBAT-BC
PBAT-CaCO3
HeatFlux (W/g)
Exo up
0
50
100
150
200
Temperature (°C)


Effect of additives on film thermal stability
Weight (%)
320
350
380
PBAT
PBAT-BC
PBAT-CaCO3
0
100
200
300
400
500
Temperature (°C)


Effect of different loadings and particle size on cooling
PBAT-BC
PBAT-Grounded-BC
PBAT-5% BC
PBAT-5% BC-CaCO3
Exo up
HeatFlux (W/g)
0
50
100
150
200
Temperature (°C)


Effect of different loadings and particle size on the first heating
PBAT-BC
PBAT-Grounded-BC
PBAT-5% BC
PBAT-5% BC-CaCO3
HeatFlux (W/g)
Exo up
60
80
100
120
140
160
180
200
Temperature (°C)


Effect of different loadings and particle size on the second heating
PBAT-BC
PBAT-Grounded-BC
PBAT-5% BC
PBAT-5% BC-CaCO3
HeatFlux (W/g)
Exo up
0
50
100
150
200
Temperature (°C)


Effect of Biochar particle size and loading on film thermal stability
Weight (%)
100
80
60
40
20
0
320
340
360
380
PBAT-BC
PBAT-Grounded-BC
PBAT-5%BC
PBAT-5%BC-CaCO3
0
100
200
300
400
500
Temperature (°C)

PBAT based composites Rheology, Arrhenius Equation

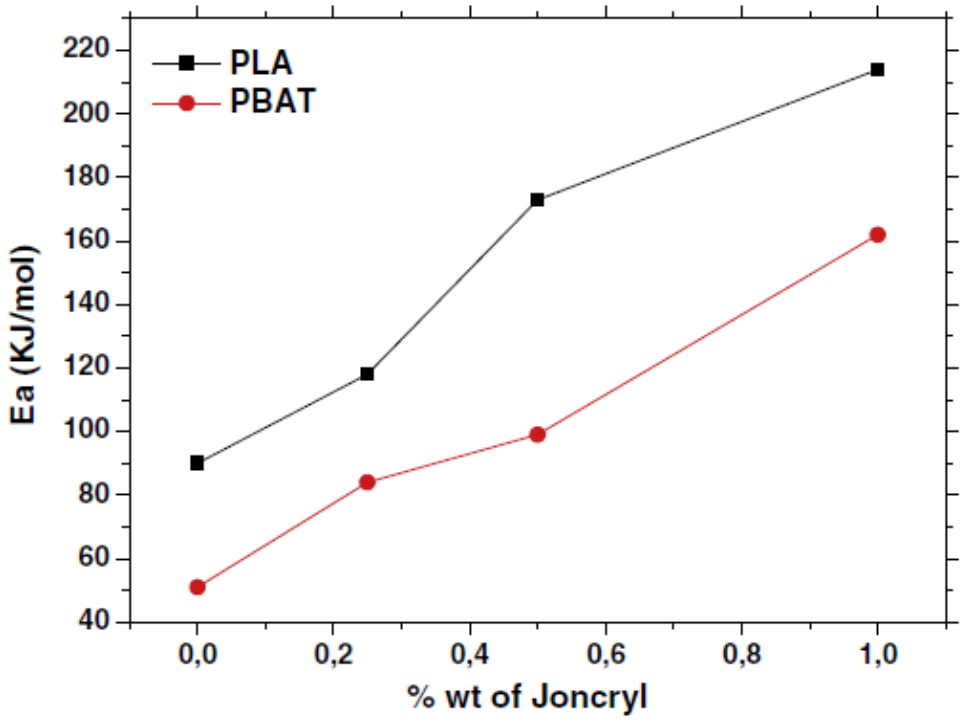
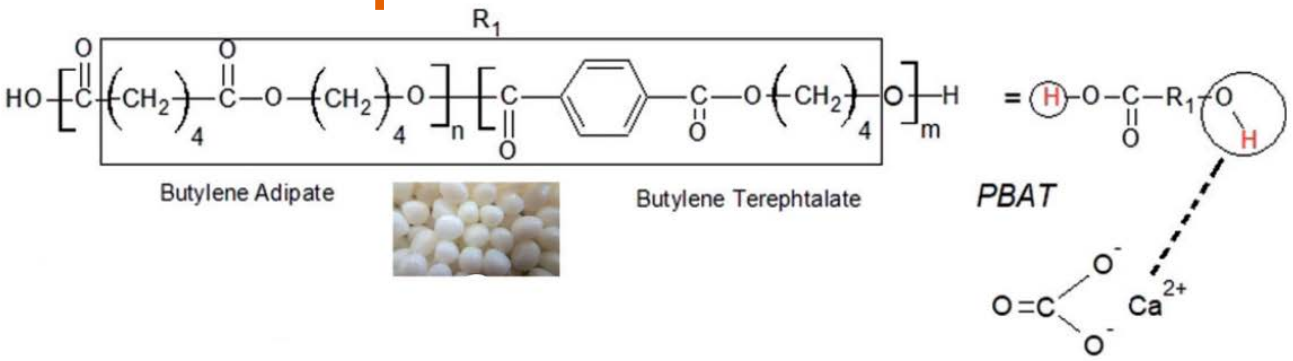


Fig. 11. Effect of long chain branching (LCB) on the activation energy.

(Al-Itry, 2014).



Reaction between Calcium Carbonate and PBAT. Adapted from (Nunes, 2020).

- Small particles, of nanoscale, are more efficient to hinder

polymer structure evolution than large ones (Al-Itry, 2014).

- No physical interactions between the matrix and the microparticles have been detected. This is attributed to the polar nature of the wood-flour particles compared with the rather hydrophobic nature of the PLA/PBAT matrix. (Georgiopoulos, 2014)

$$|\eta^*| = A^\circ \exp\left(-\frac{E_a}{RT}\right)$$