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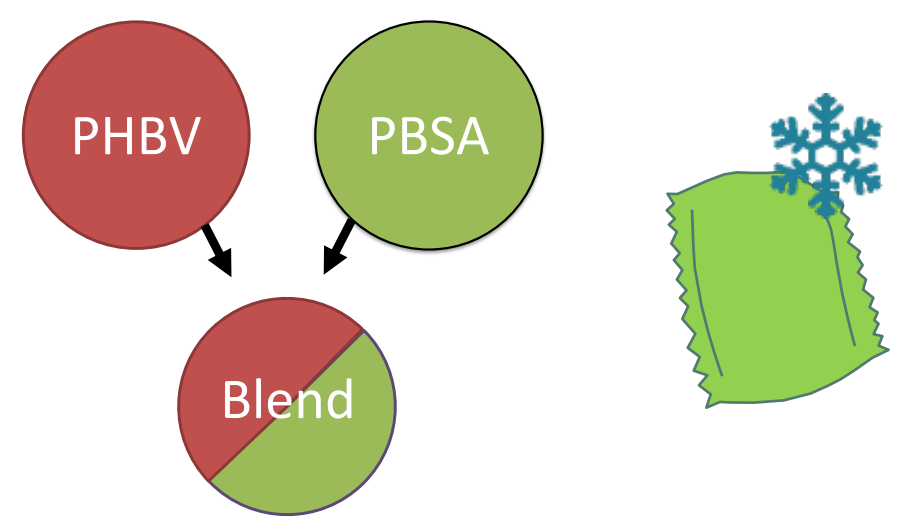
# Nucleation of biodegradable poly(hydroxybutyrate-co-hydroxyvalerate) and poly(butylene succinate-co-adipate) blends

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## Introduction

**Objective: Nucleation of PHBV in biobased and biodegradable polymer blends for the packaging of frozen food**



Polyhydroxyalkanoates (PHAs) are thermoplastic polyesters produced as carbon and energy storage compounds by microorganisms under nutritional stress. Short-chain-length PHAs, mainly represented by poly(3-hydroxybutyrate) P(3HB) and the copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate)P(3HB-co-3HV) are already commercially available. PHBV can be produced using carbon sources from waste or by-products of agriculture and food industries. This would further promote circular economy because local food waste could be used to make food containers. PHBV is a stiff, brittle, highly crystalline polymer with low thermal stability and a narrow processing window. One strategy that can be adopted to overcome these drawbacks is based on physical melt-blending using compatibilizers. We developed PHBV/PBSA blends compatibilized with dicumyl peroxide (DCP). PHBV forms large spherulites during annealing treatment, which are not beneficial for its mechanical properties. Therefore, nucleating agents, such as boron nitride, BN, are commonly used. They increase the nucleation density and help the yield more and smaller spherulites. Here the nucleation of PHBV in compatibilized blends with PBSA with BN and its consequences were investigated.

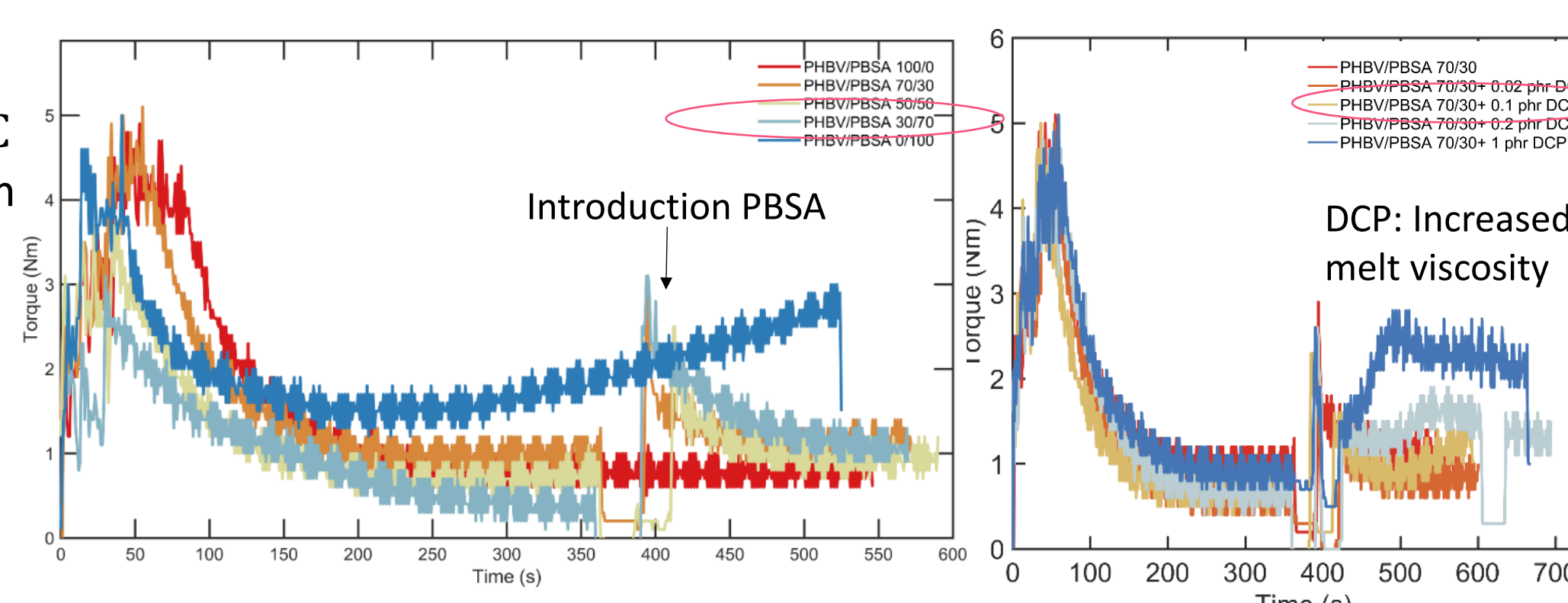
## Blend processing

### Development of the compatibilized blend using an internal mixer

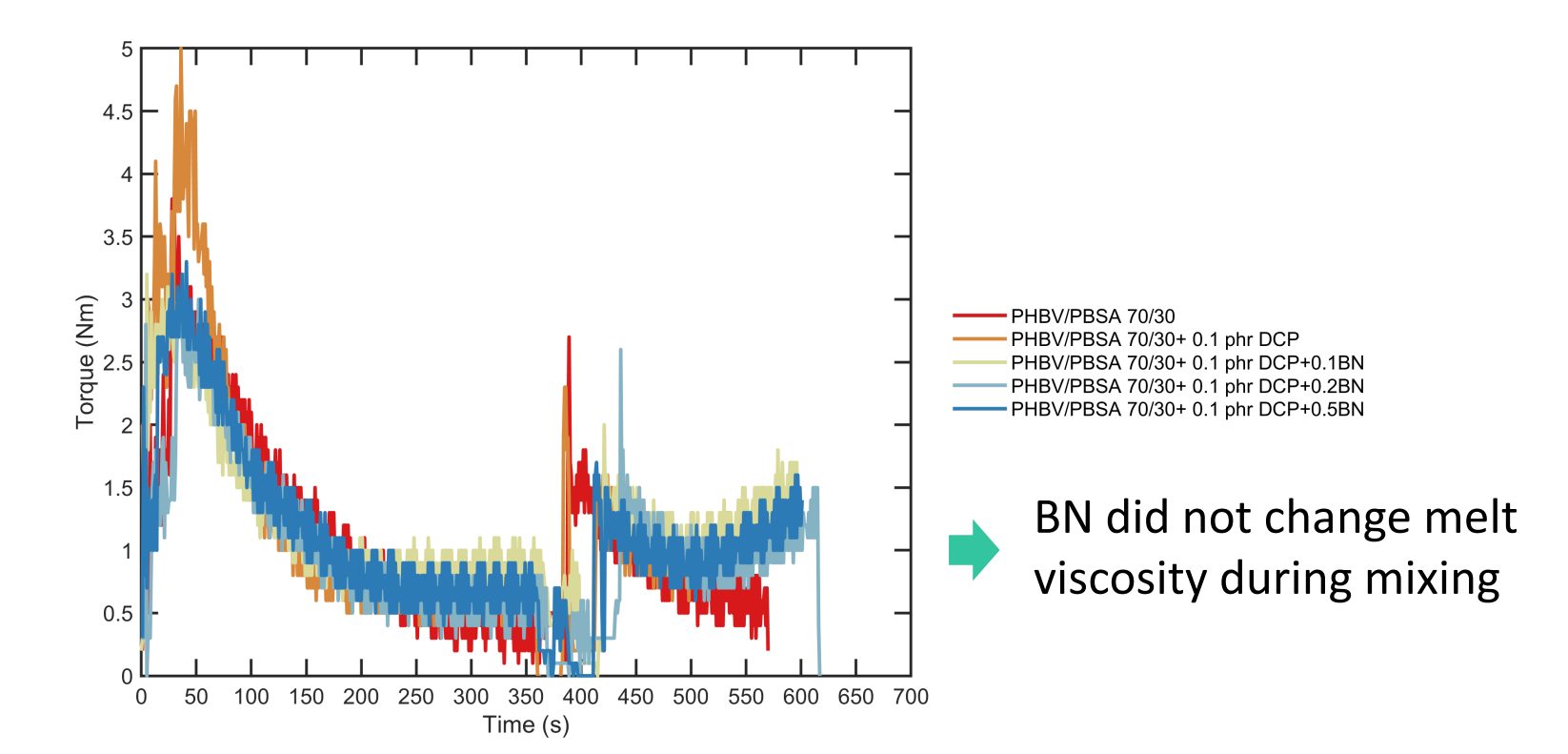


Blending:  
 ○ Temperature: 190°C  
 ○ Screw speed: 90rpm  
 ○ Time: 9'

Sample film fabrication:  
 Thermo-compression at 180 °C, 150 bar

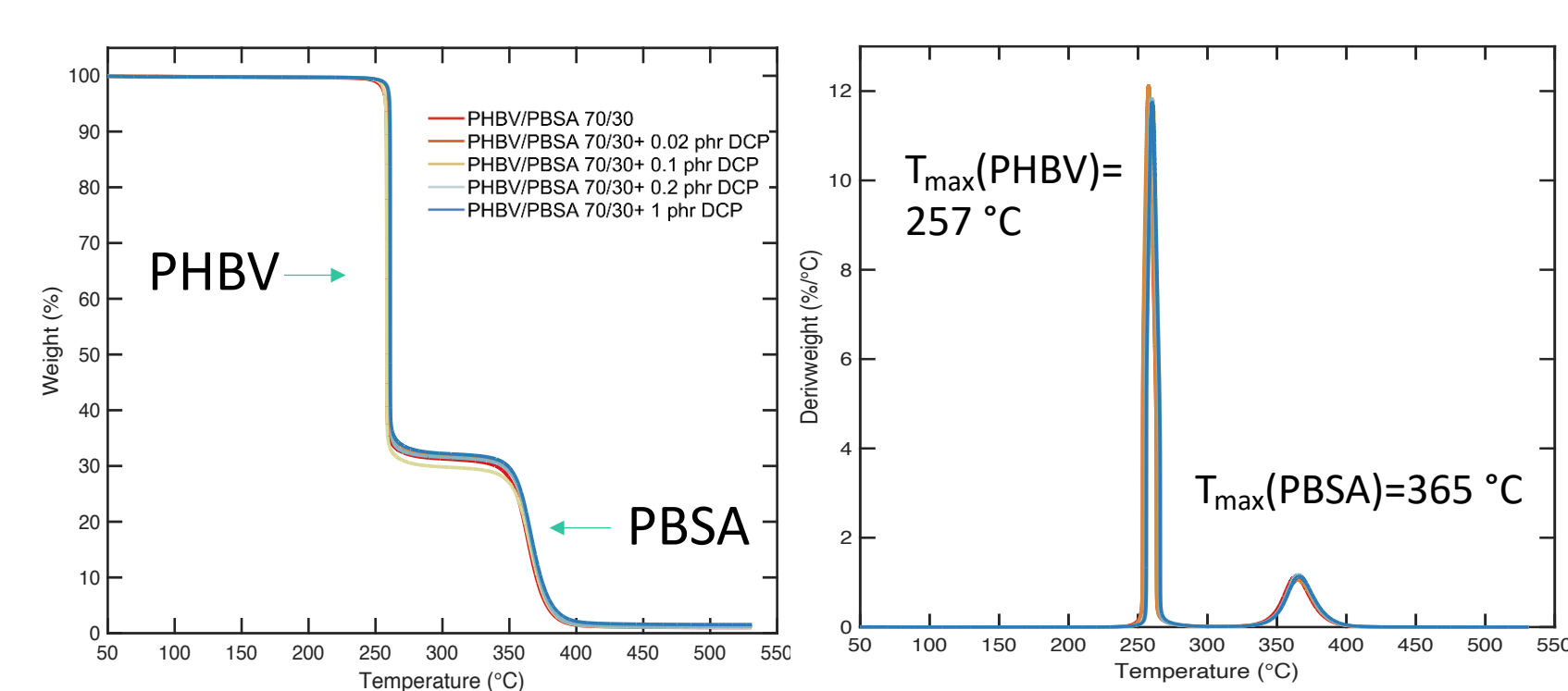


### Addition of BN as nucleating agent



## Results

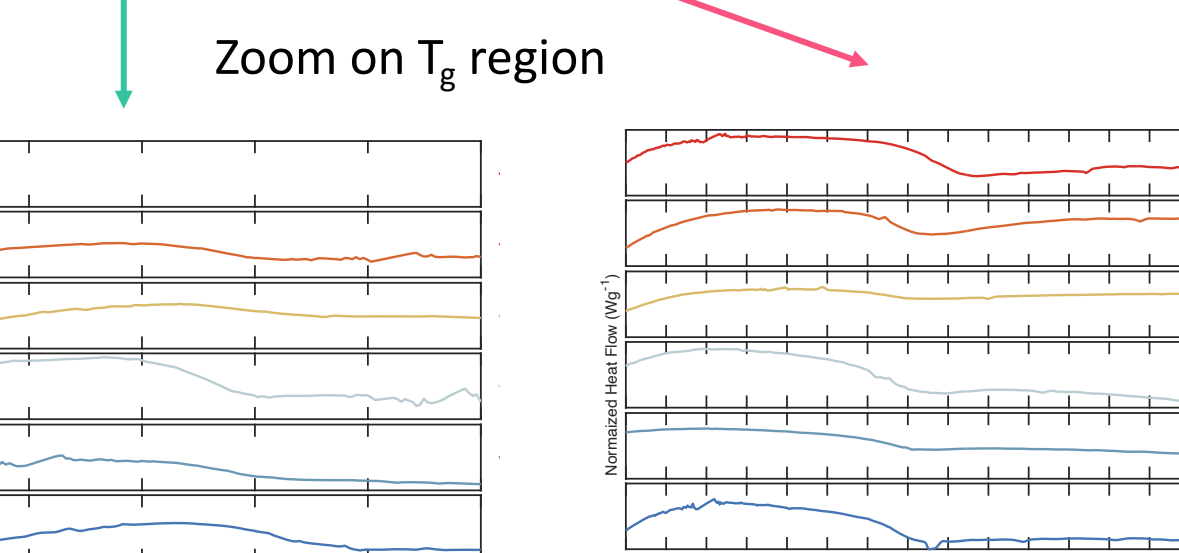
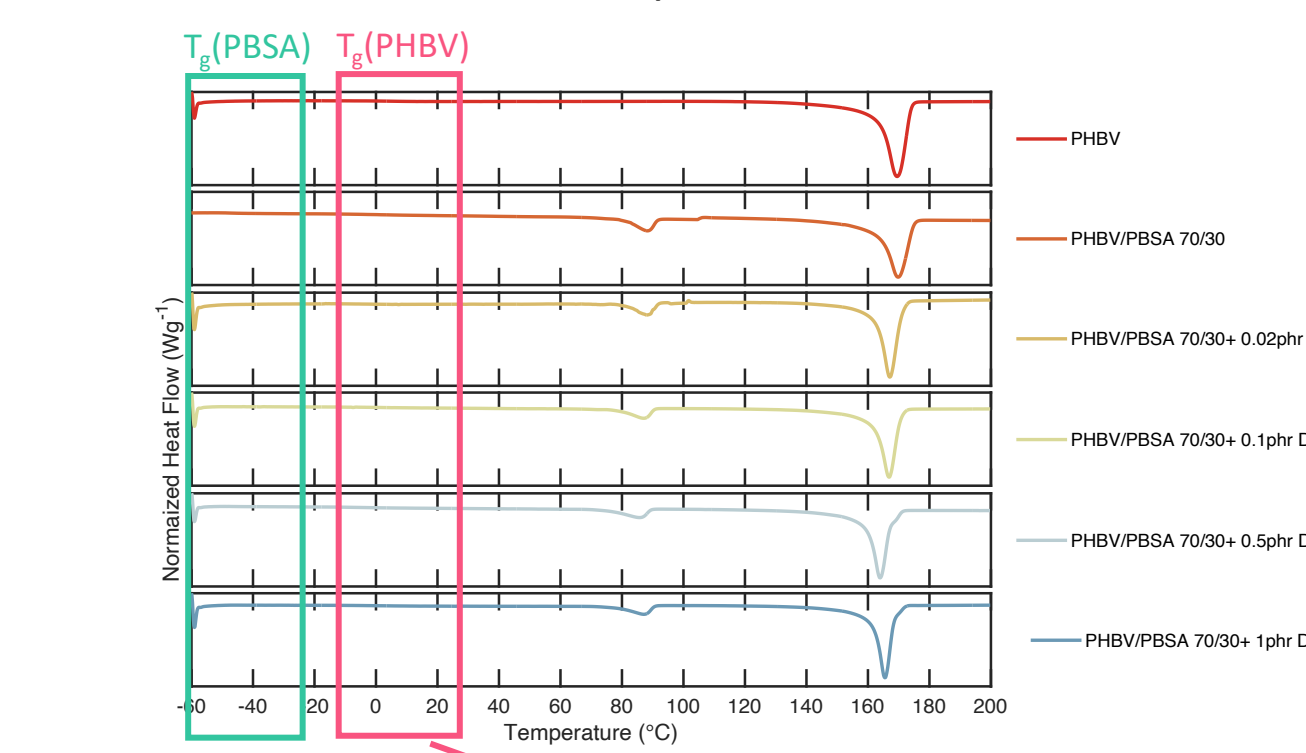
### Thermal stability of PHBV/PBSA+ 0.1 phr DCP with BN



- Quantity of PBSA and PHBV confirmed
- Quantity of BN confirmed
- DCP and BN do not change degradation temperature.

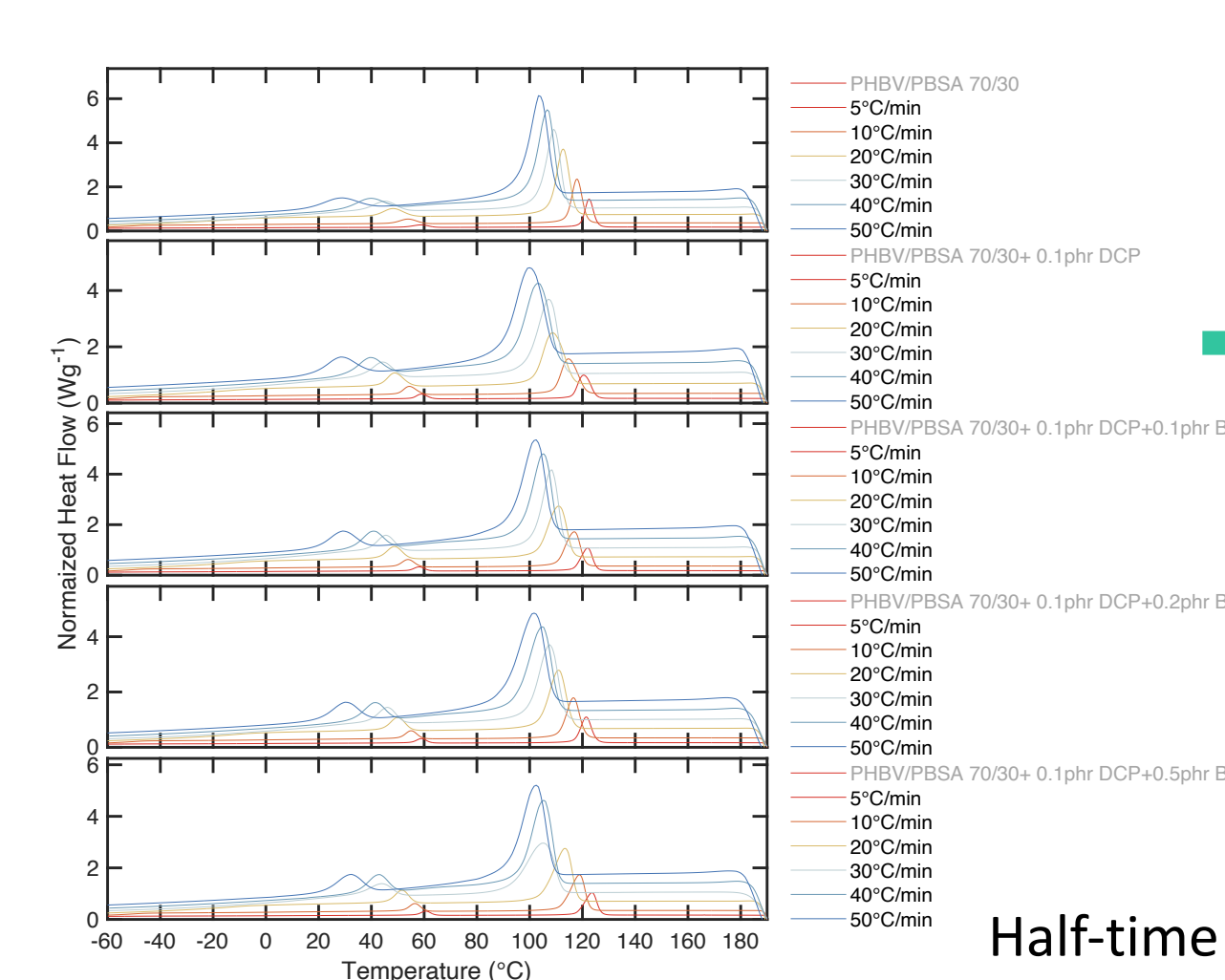
### Analysis of non-isothermal crystallization kinetics

Glass transition of PHBV/PBSA blends + DCP

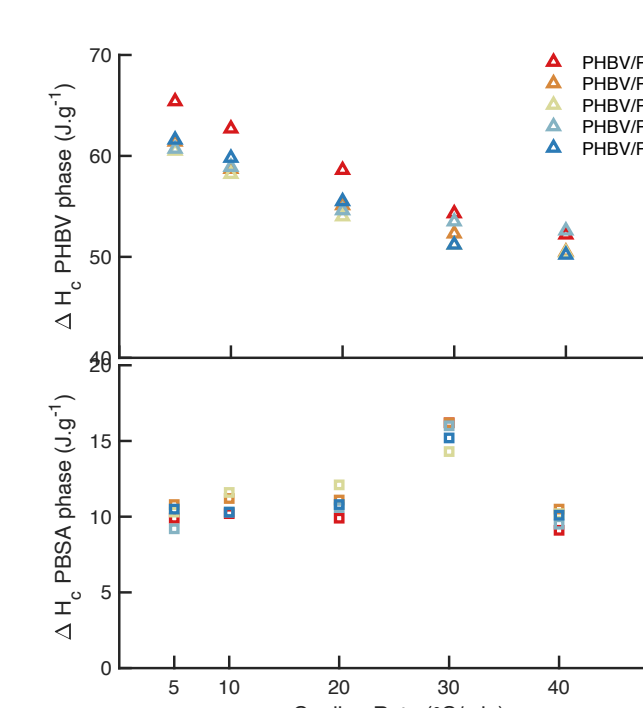


- Two distinct glass transition temperatures: PBSA and PHBV
- T<sub>g</sub> almost unchanged whatever blend ratio
- > PHBV and PBSA are immiscible.

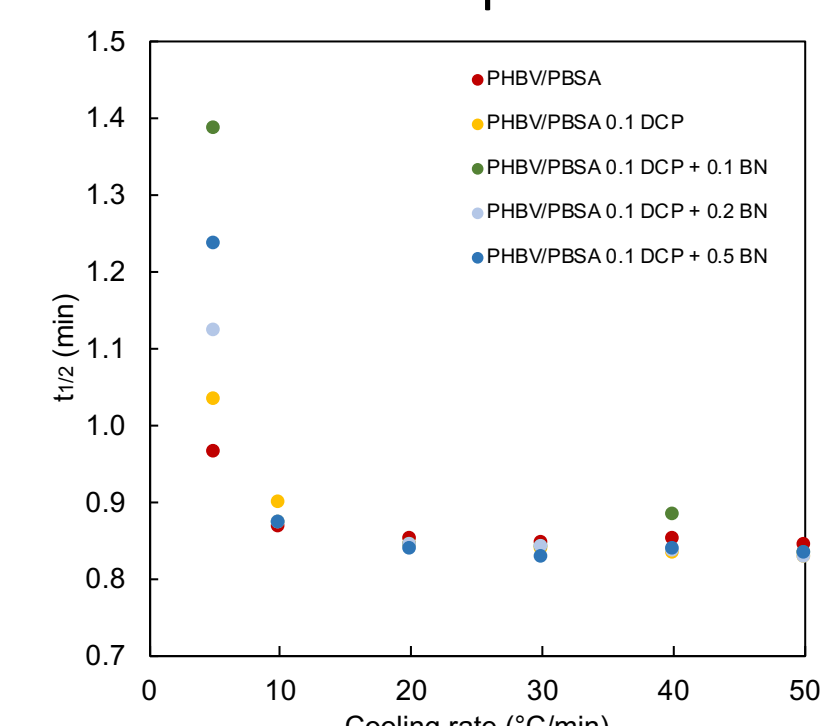
Nucleation of PHBV/PBSA blends + 0.1 phr DCP



Analysis of the non-isothermal crystallization kinetics with the Avrami-Jezorny equations

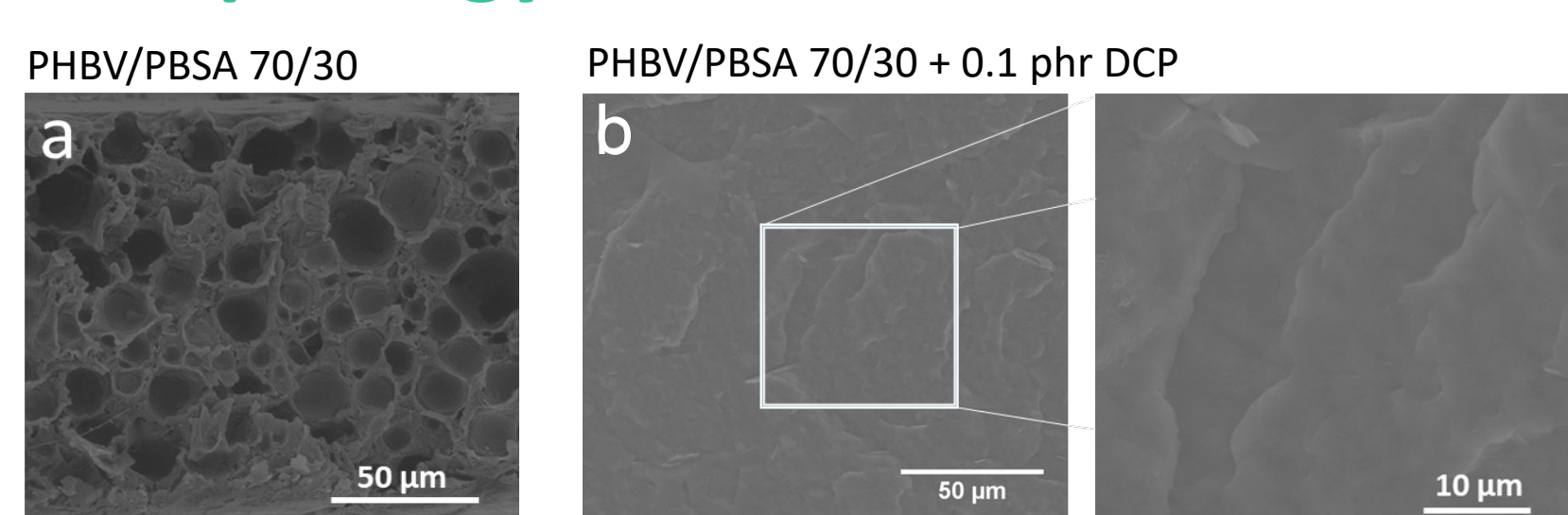


Half-time of crystallization of the PHBV phase



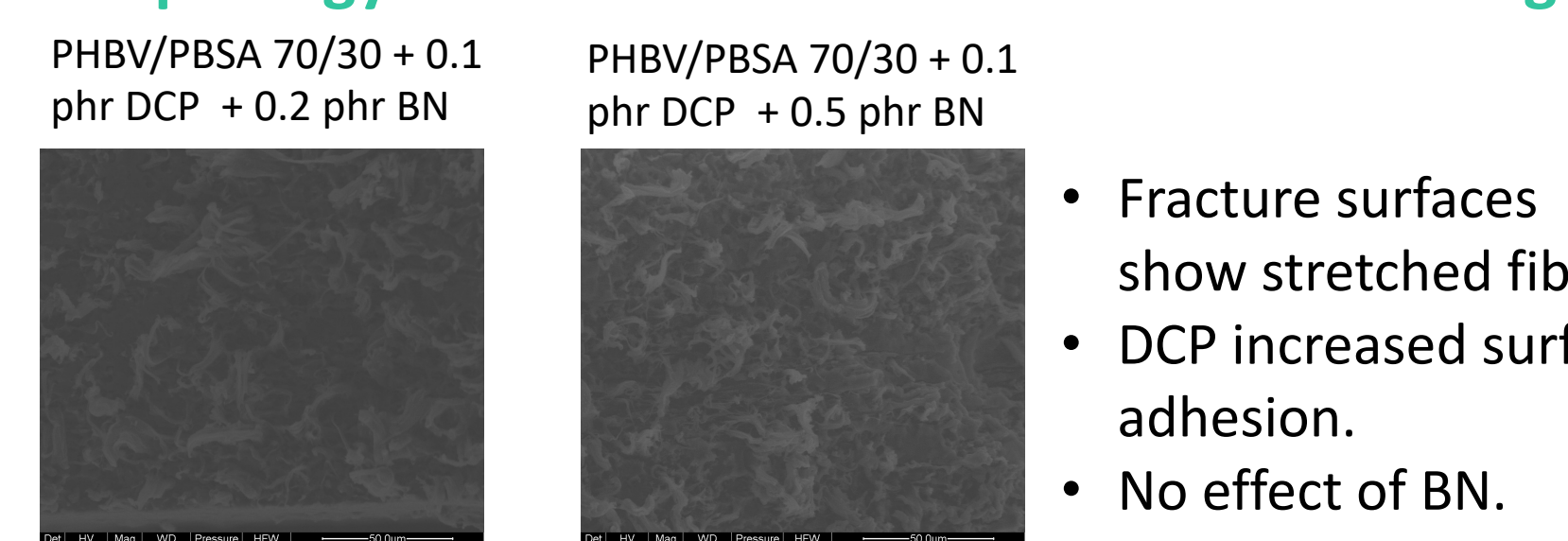
- At the tested concentrations, BN had no supplementary nucleating effect on the PHBV phase.

### Morphology of PHBV/PBSA/DCP blends



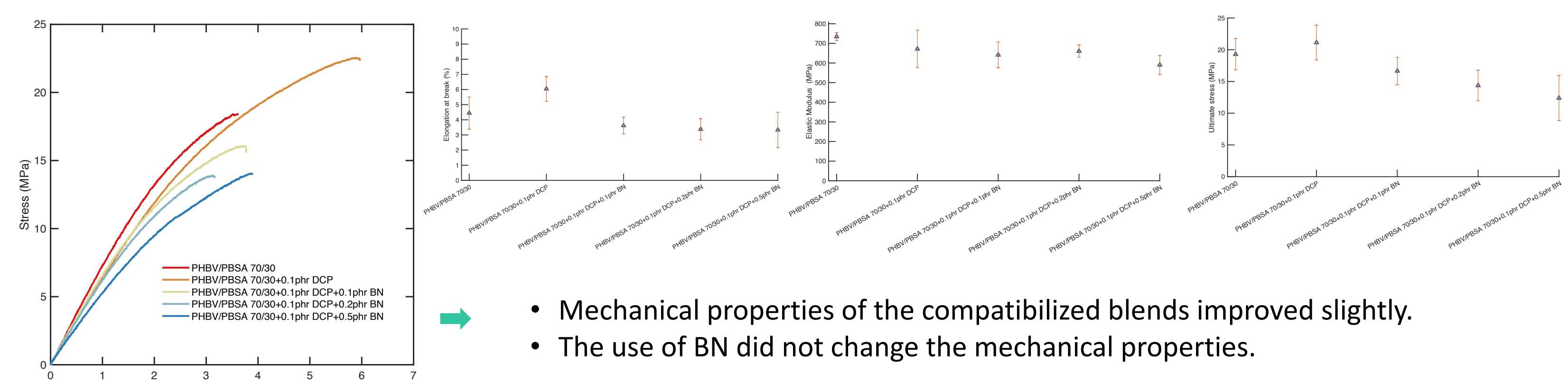
DCP decreased size of PBSA nodules in PHBV.

Morphology of fracture surfaces after tensile testing



- Fracture surfaces show stretched fibers.
- DCP increased surface adhesion.
- No effect of BN.

### Mechanical properties of the films in service situation



- Mechanical properties of the compatibilized blends improved slightly.
- The use of BN did not change the mechanical properties.

## Conclusions

This study investigated the *in-situ* compatibilization and nucleation of PHBV/PBSA blends at a weight ratio of 70:30 using the free radical initiator dicumyl peroxide (DCP) and the nucleant BN. Batch mixing was used for the fabrication of different formulations and test samples were produced by thermo-compression. PHBV and PBSA are immiscible. The addition of DCP induced reaction between PHBV and PBSA leading to the formation of a cross-linked PHBV-g-PBSA structure acting as compatibilisant. The size of the PBSA nodules in the compatibilized blends decreased. The use of DCP had no impact on the thermal properties of the polymers. Nucleation by BN did not affect the half-time of crystallization. The results of tensile testing showed that the elongation at break slightly increased with addition of DCP. The observation of the fracture surface showed some stretched fibers. However, no evolution of the elastic modulus or the ultimate stress was found. The use of BN in the tested concentration was disadvantageous for the mechanical properties. In conclusion, the compatibilizing of PHBV/PBSA blends with DCP was promising, but no advantage of supplementary nucleation for the properties of the blends was observed.

## REFERENCES

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- Le Delliou, B., Vitrac, O., Domenek, S., "Agricultural, Forestry and Bioindustry Biotechnology and Biodiscovery" Chong, P. A., Newman, D. J., Steinmacher, D. A., Eds. Springer International Publishing: Cham, **2020**, 227.