



# Effect of halloysite nanotubes on the morphology and the crystallization of immiscible poly (hydroxybutyrate-co-valerate) (PHBV)/ poly (butylene succinate) (PBS) blends.



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# \* Introduction

synthetic plastics



Google images

Development of Biodegradable resources

Poly (hydroxybutyrate-co-valerate)  
*PHBV*

- High cost,
- Brittleness
- Thermal instability,

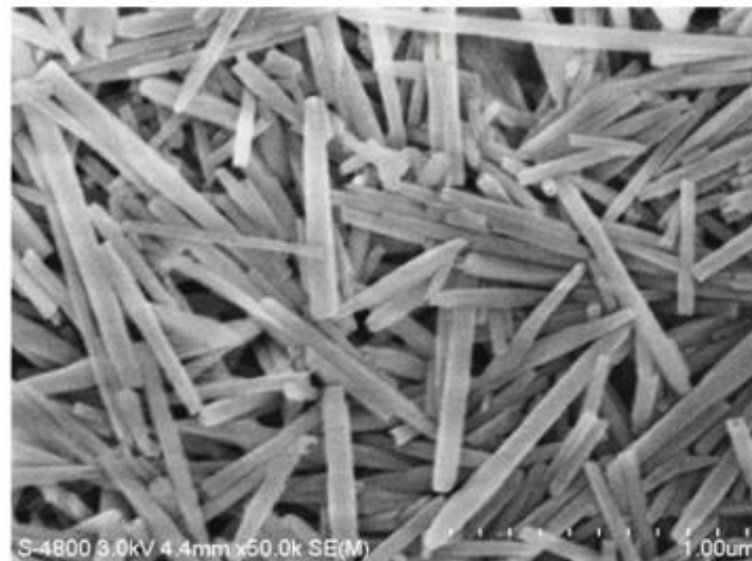
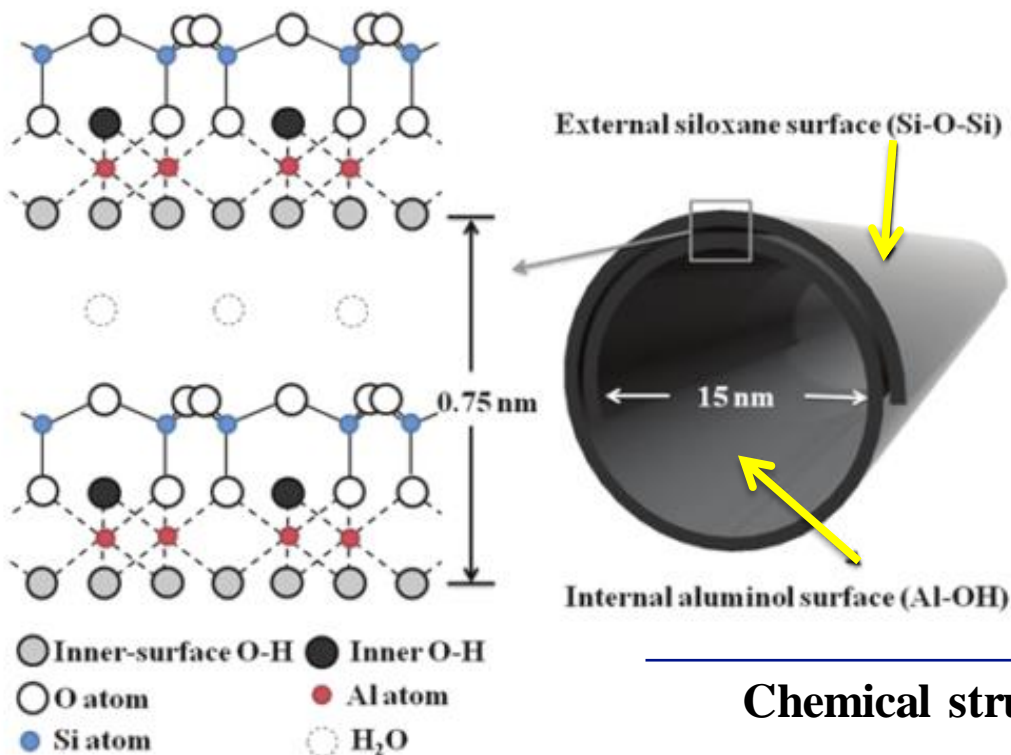
Polymer Blending  
poly (butylene succinate) (*PBS*)

Microstrural modification

Block grafted copolymers

Inorganic material:  
Clays (halloysite)

# Halloysite (HNT)



**Chemical structure**

**$(\text{Al}_2 \text{Si}_2 \text{O}_5 (\text{OH})_4 n\text{H}_2\text{O})$**

Inner diameter

10-40 nm

Outer diameter

40-70 nm

Length

0.2-2 $\mu\text{m}$

Aspect ratio (L/D)

10-50

Mingxian Liu et al. *Progress in Polymer Science* 39 (8). 1498–1525 (2014).

Weng On Yah et al. *Journal of the American Chemical Society* 134 (3), 1853–59 (2012).

**Some works on the PHBV (PHB) /PBS blends were focused on the:**

- Miscibility and crystallization behavior of PHBV/PBS blends**
- Using Dicumyl Peroxide as a Free-Radical Grafting Initiator and compatibilizer.**

- Piming Ma et al. *Macromol. Mater. Eng.* **297**, 402–410 (2012).
- Piming Ma et al. *Journal of Applied Polymer Science*, *41020*, (2014). doi:10.1002/app.41020

**Only rare studies are available on the effects of HNT on the properties of PHBV/polymer blends.**

- Paola Scarfato et al. *Polymer Composites*, *16*, (2015). Doi: 10.1002/pc.23478

**No publications are available on the use of HNT or PHBV-g-MA as compatibilizers for PHBV/PBS blends**

*\* Objectives*

**Study of the morphology and thermal properties of PHBV/PBS binary blends.**

**Study of the effect of HNT and PHBV-g-MA on the morphology and thermal stability of PHBV/PBS 80/20 binary blend.**

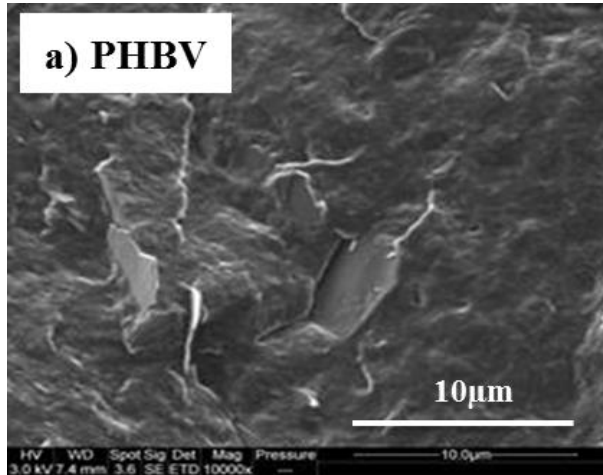
**\*Materials and processing**

<b>Sample</b>	<b>HNT (wt.%)</b>	<b>PHBV-g-MA (wt.%)</b>
<b>PHBV</b>	–	–
<b>PHBV/PBS 80/20</b>	–	–
<b>PHBV/PBS 50/50</b>	–	–
<b>PHBV/PBS 20/80</b>	–	–
<b>PBS</b>	–	–
<b>PHBV/PBS 80/20 + 5PHBV-g-MA</b>	–	5
<b>PHBV/PBS 80/20 +5HNT</b>	5	–
<b>PHBV/PBS 80/20 +5HNT+5PHBV-g-MA</b>	5	5

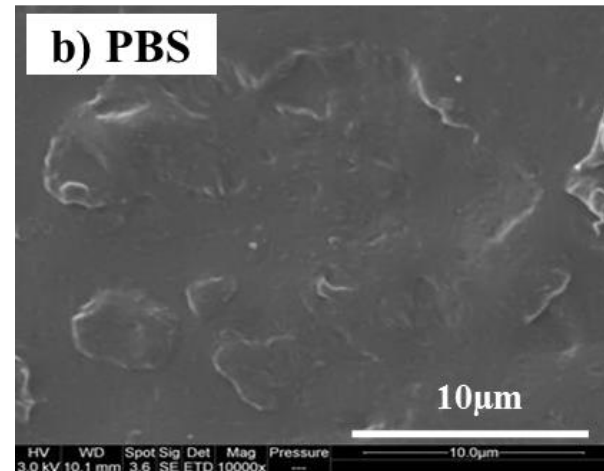
# Study of the morphology and thermal properties of PHBV/PBS binary blends

✱ SEM analysis on cryofractured surfaces

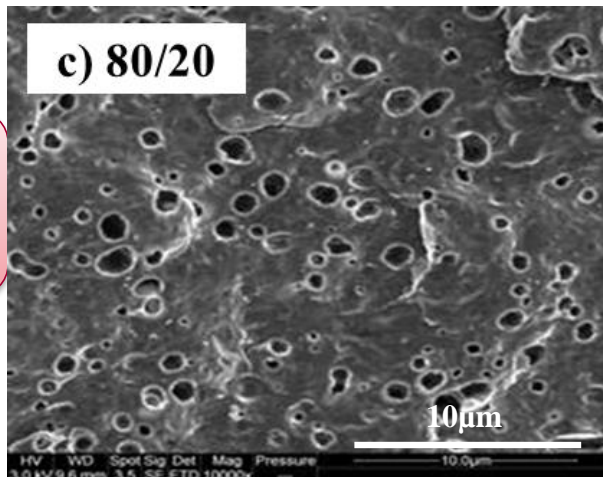
Irregular surface



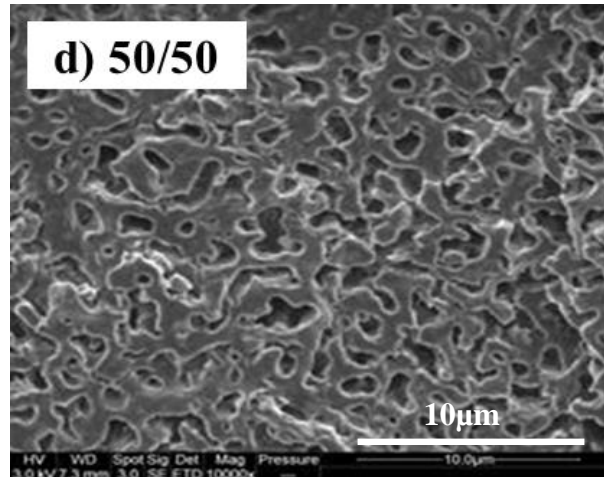
Smooth surface



Nodular structure



Co-continuous morphology

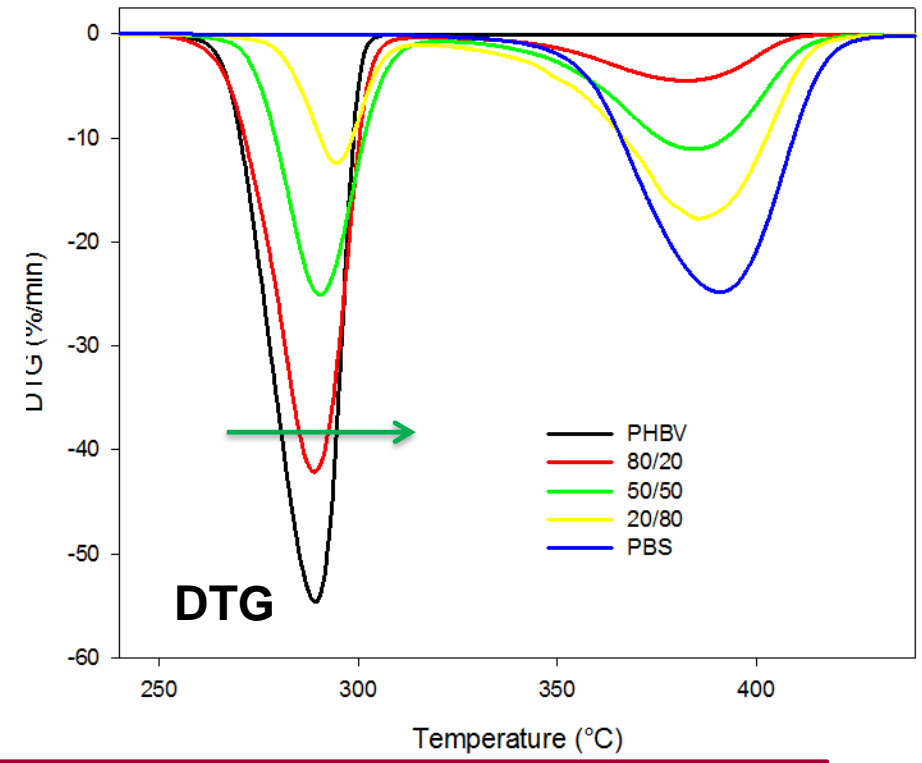
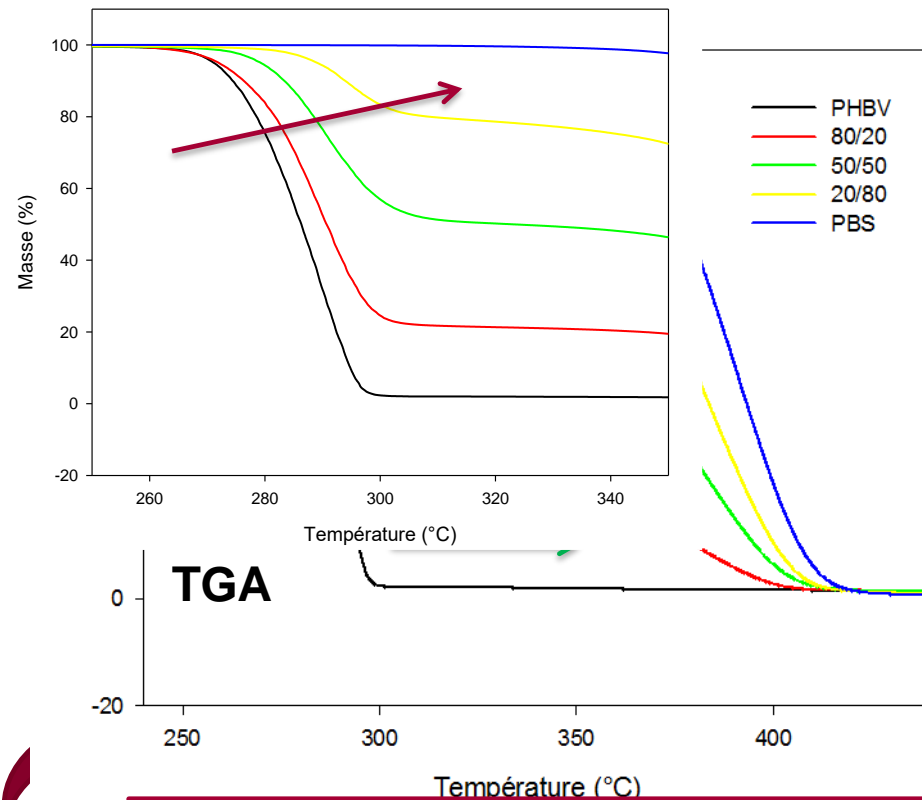


SEM micrographs of PHBV/PBS blends after selective dissolution of PBS in chloroform at room temperature for 1h



✳ Thermogravimetric analysis (TGA)

- SETSYS EVOLUTION, SETARAM, France
- 10 °C/min, N<sub>2</sub> at 20 ml/min



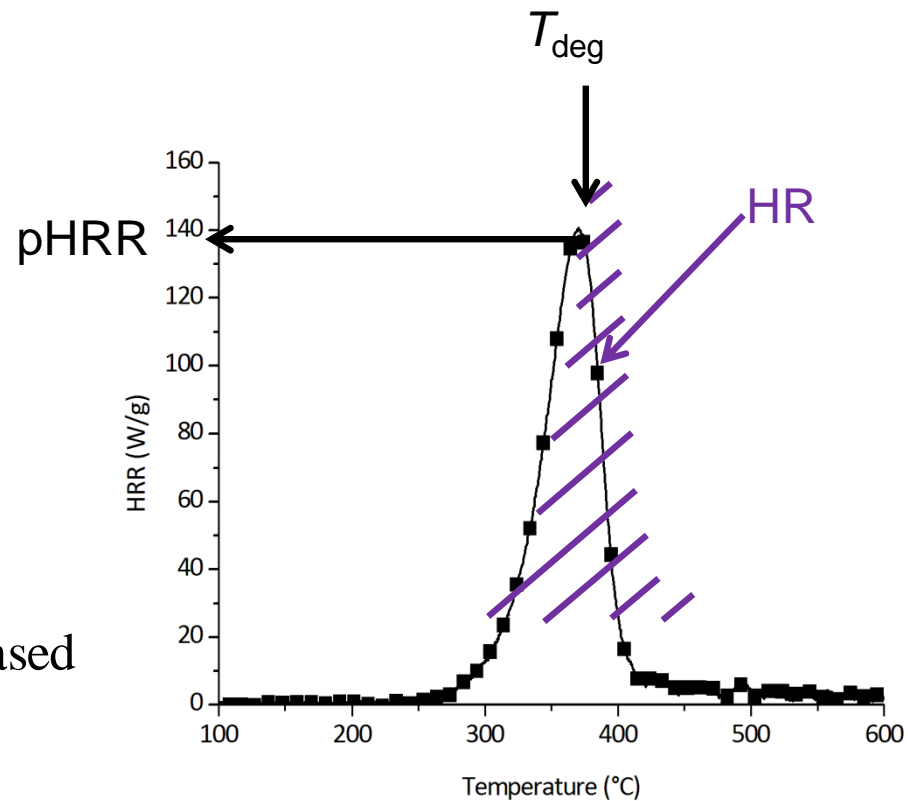
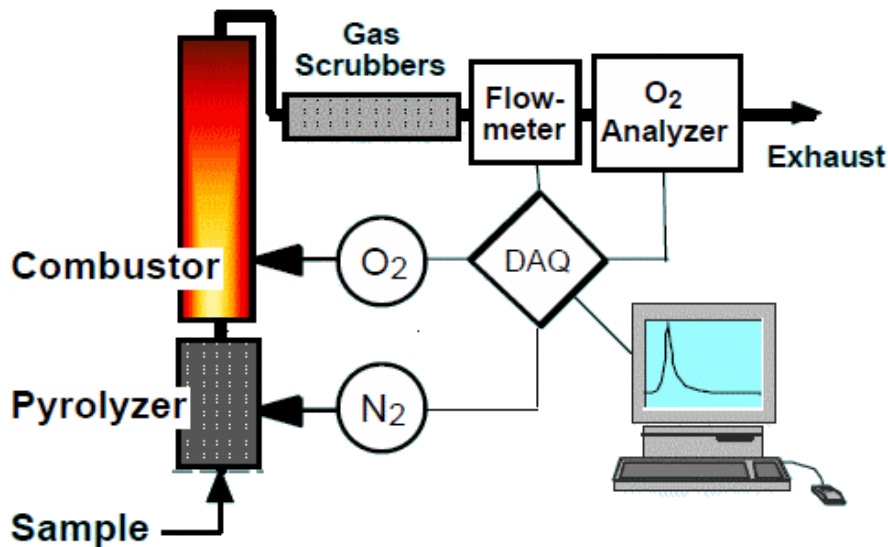
- PHBV is more thermally stable than PHBV
- The blends show two weight loss steps: first and second are attributed to PHBV and PBS respectively

- PHBV provides an enhancement of the thermal stability of PHBV.

## Experimental Study of Fire Reaction (Microscopic Scale)

1°C/s

Sample weight : ~2mg



$$EHC = \frac{HR}{ML}$$

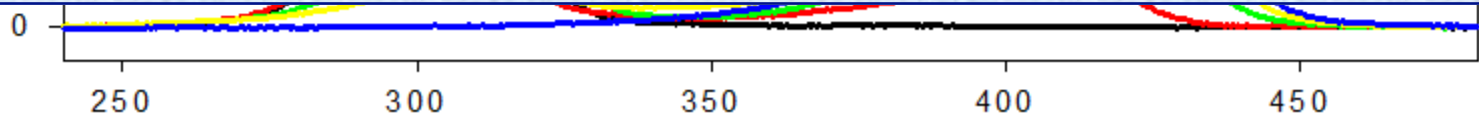
Heat Released  
Mass Loss

Effective Heat Capacity



PCFC results for pure polymers and PHBV/PBS blends

Samples	pHRR <sub>PHBV</sub> (W/g)	pHRR <sub>PBS</sub> (W/g)	HR <sub>PHBV</sub> (kJ g <sup>-1</sup> )	HR <sub>PBS</sub> (kJ g <sup>-1</sup> )	THR <sub>blend</sub> (kJ g <sup>-1</sup> )
PHBV	1027 ± 77.2	—	20.6 ± 0.84	—	—
80/20	702.5 ± 37	72.1 ± 2.1	16.4 ± 0.1	3.6 ± 0.1	19.8 ± 0.45
50/50	390 ± 18.4	176.6 ± 7	10.4 ± 0.7	10.1 ± 0.8	20.3 ± 1.24
20/80	298.7 ± 11	303.8 ± 11	4.7 ± 0.2	15.2 ± 1.3	19.5 ± 0.91
PBS	—	426.15 ± 20	—	14.2 ± 0.5	—



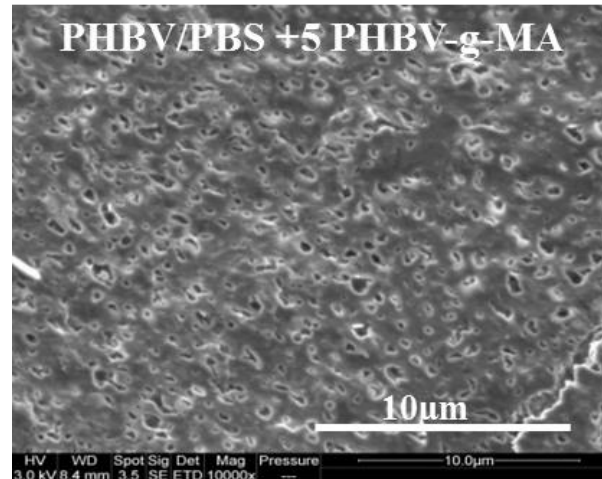
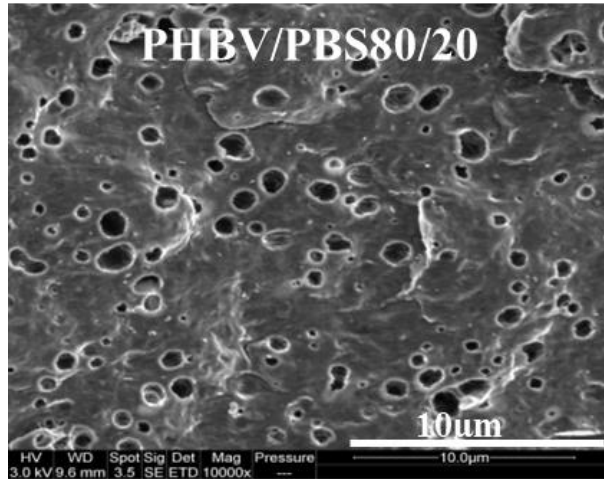
-71%

- Large reduction in the peak heat release rate (HRR) with adding PBS (-71%),
- Fire behavior of blends is improved with PBS content.

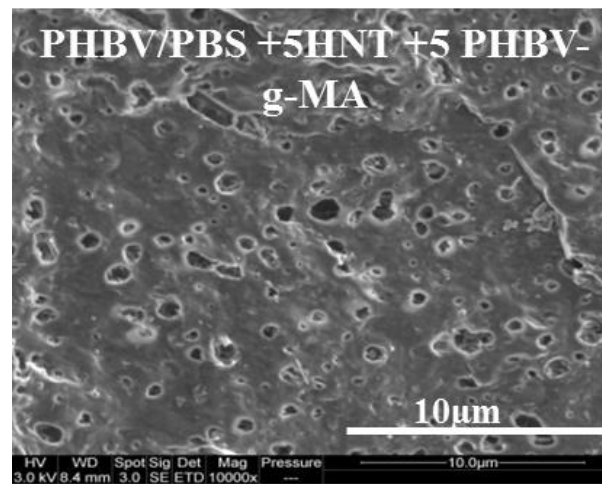
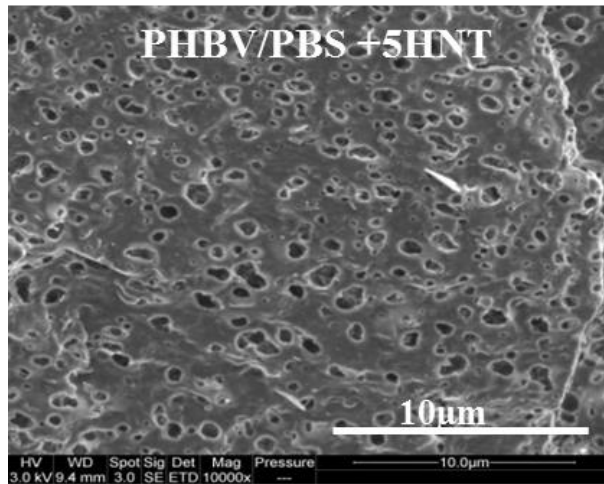
# Effect of HNT and PHBV-g-MA on PHBV/PBS 80/20 binary blend.

- The PHBV/PBS ratio was 80/20
- Filler content was 5wt.%
- PHBV-g-MA was added at 5wt.%

**SEM**

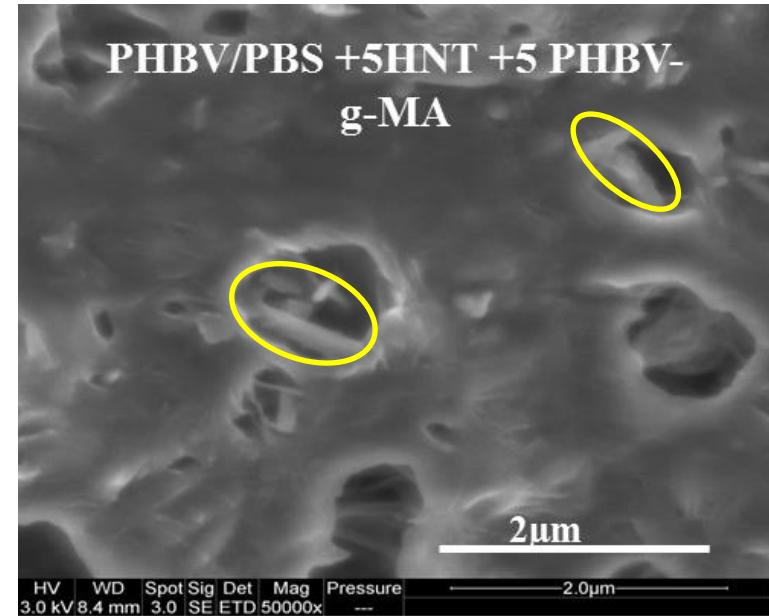
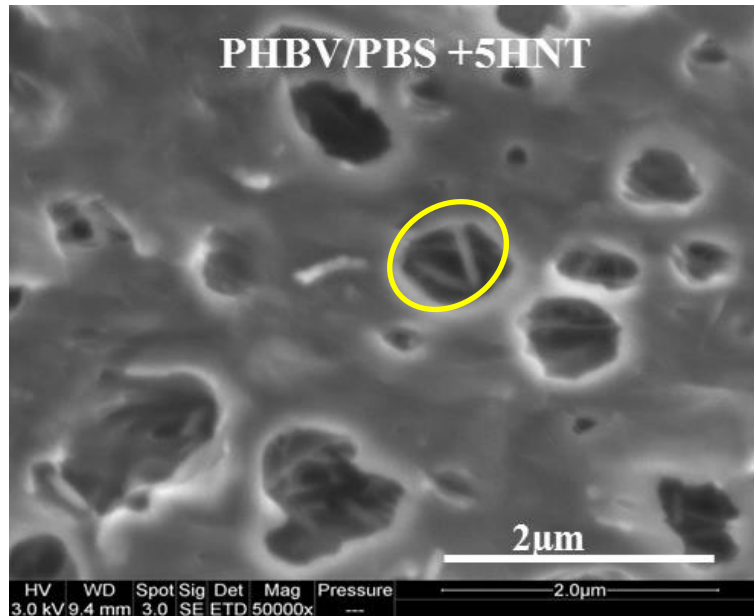


Dispersion effect of PHBV-g-MA by reducing interfacial tension



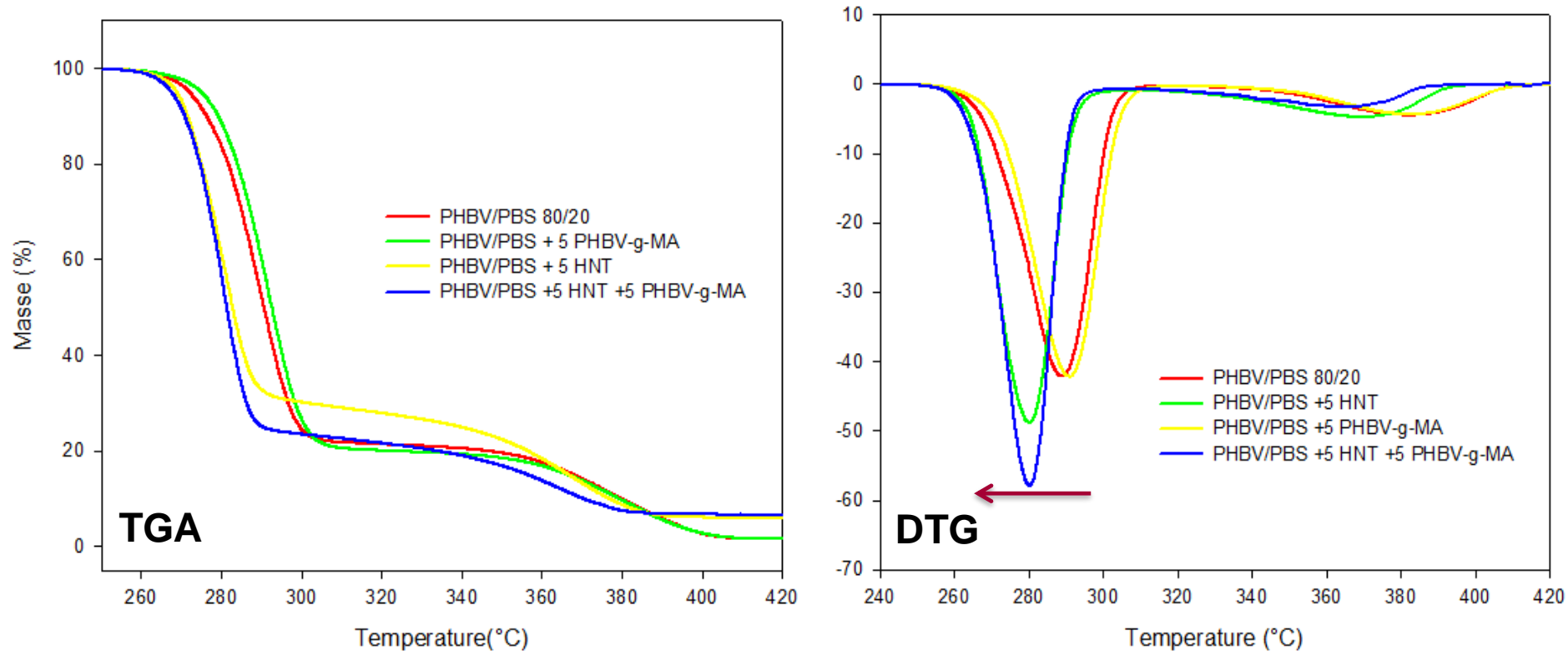
Limited dispersion effect when adding HNT and HNT+PHBV-g-MA

## Localization of HNT in the PHBV/PBS blends



Apparently, most of the HNT particles are located in PBS domains.  
 Less HNTs are found in PHBV phase  
 → This suggests a better affinity of clay for PBS than for PHBV

## \* TGA analysis



- PHBV-g-MA does not influence the thermal stability of PHBV in the 80/20 blend .
- The addition of HNT in neat blend and its combination with PHBV-g-MA required lower thermal stability.

**→HNT reduces the thermal stability of nanocomposites**





## PCFC parameters of 80/20 nanocomposites blends

800

Samples	pHRR <sub>PHBV</sub> (W/g)	pHRR <sub>PBS</sub> (W/g)	HR <sub>PHBV</sub> (kJ g <sup>-1</sup> )	HR <sub>PBS</sub> (kJ g <sup>-1</sup> )	THR <sub>blend</sub> (kJ g <sup>-1</sup> )
PHBV	1027 ± 77	–	–	–	20.6±0.8
80/20	702.5 ± 37	72.1 ± 2.1	16.4 ± 0.1	3.6 ± 0.1	19.8 ± 0.5
5PHBV-g-MA	779 ± 19	51.6 ± 0.6	14.7 ± 0.5	3.5 ± 0.5	18.4 ± 0.2
5 HNT	594,3 ± 3	86 ± 1.5	14.4 ± 0.2	5 ± 0.3	19.7 ± 0,3
5HNT-5PHBV-g-MA	738.6 ± 19	77.5 ± 11	16.2 ± 0.6	3.7 ± 0.4	19.6 ± 0.6
PBS	426.1±20	26.15 ± 2	–	–	14.2 ± 0.5

- pHRR is about -15,4% lower in presence of HNT than for neat PHBV/PBS 80/20
- The pHRR increased when HNT is filled together with PHBV-g-MA. This is due an adverse effect of PHBV-g-MA on thermal stability.



## *\*Conclusions*

- ✚ **Immiscibility of biodegradable PHBV/PBS blends prepared by melt compounding was studied by SEM.**
- ✚ **TGA and PCFC test show that blending PBS with PHBV contributes to the improvement of thermal stability and flame retardancy of the blends,**
- ✚ **The addition of compatibilizer remarkably refined the morphology of the 80/20 wt. ratio blend. The addition of PHBV-g-MA does not affect the thermal stability.**
- ✚ **The use of HNT and its combination with PHBV-g-MA shows limited dispersion effect. Thermal stability of 80/20 blend decreases with addition of HNT. Nevertheless, HNT seems to play a positive effect on flame retardancy.**
- ✚ **The combination of HNT and PHBV-g-MA leads to a similar fire behavior as neat 80/20 blend.**

## Acknowledgments



EGIDE , TASSILI (PHC Hubert Curien)  
program N°13 MDU 891



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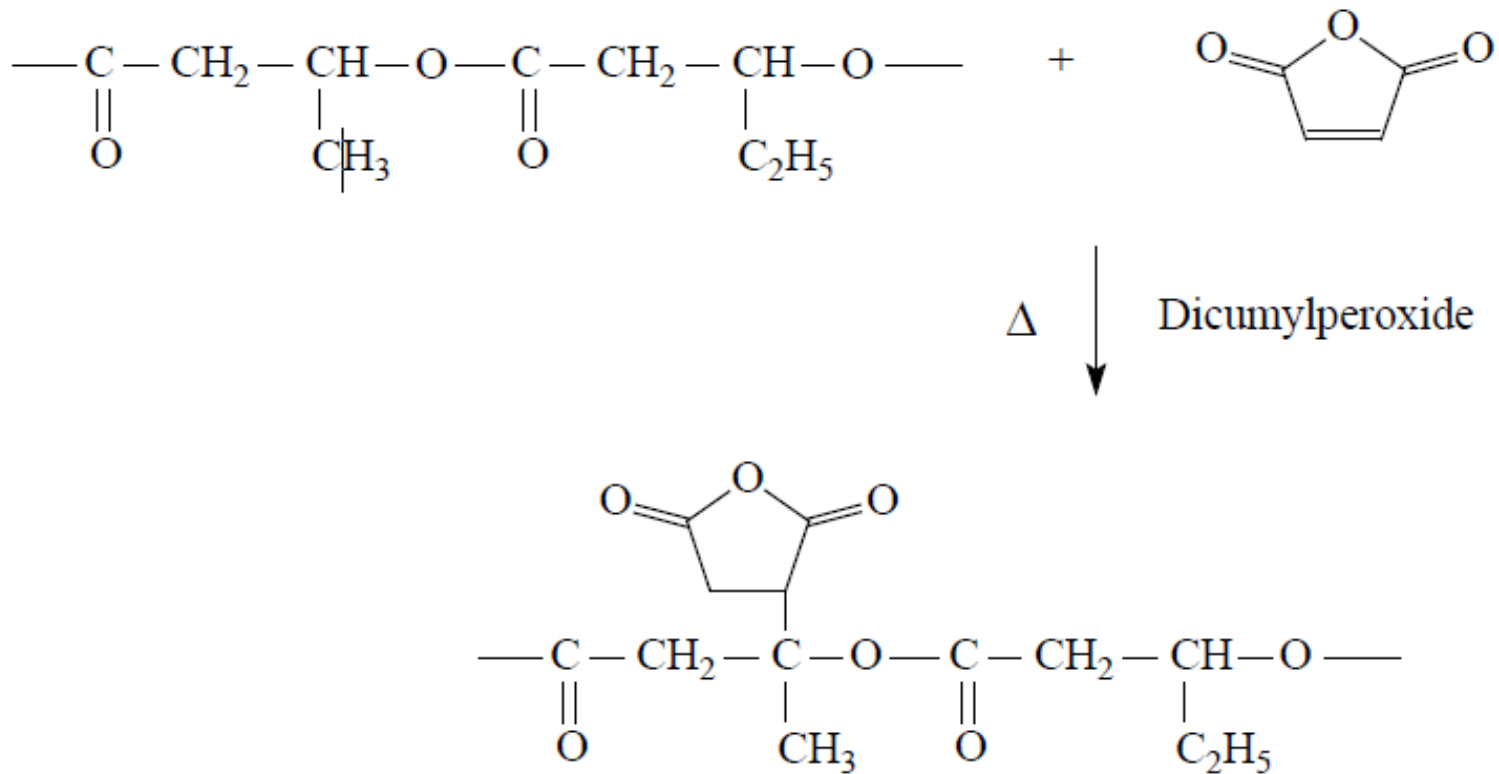


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(LPIM),

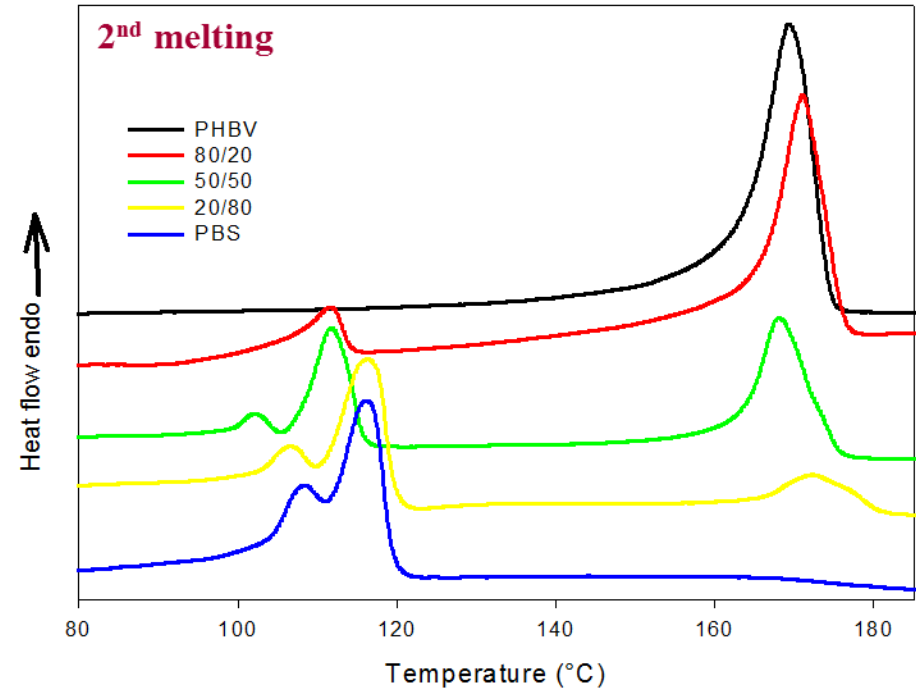
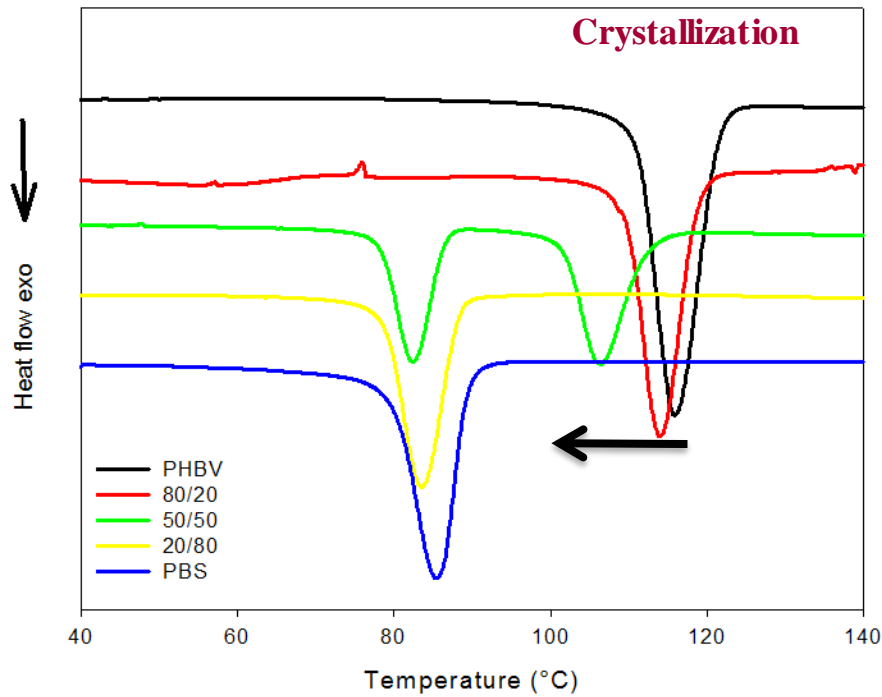


**THANKS' FOR YOUR  
ATTENTION**





Grafting of Maleic anhydride onto PHBV



- A decrease in  $T_c$  of PHBV with increasing PBS content is noted.
- $T_c$  peak of PBS and PHBV disappears in the blends 80/20 and 20/80, respectively (co-crystallization of PHBV and PBS is suggested).
- Melting behavior of PHBV is not affected by PBS content, whereas  $T_m$  of PBS is slightly decreased with high content of PHBV.

Samples	PHBV					PBS				
	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (W/g)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (W/g)	X <sub>c</sub> (%)	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (W/g)	T <sub>m</sub> (°C)	ΔH <sub>f</sub> (W/g)	X <sub>c</sub> (%)
<b>PHBV</b>	115,7	83,4	169	88,4	60,	–	–	–	–	–
<b>PHBV/PBS 80/20</b>	113,20	62,88	170,5	69,4	59,4			111,4	11,6	29
<b>PHBV/PBS 50/50</b>	107,7	36	168,4	42	57,5	81,9	27,3	111,9	28,5	28,5
<b>PHBV/PBS 20/80</b>			170,5	11,9	40	81,8	50,64	114,4	46,9	29,3
<b>PBS</b>	–	–	–	–	–	85,93	58,55	115	60,4	30