Fire retardant behaviour of polylactide nanocomposites

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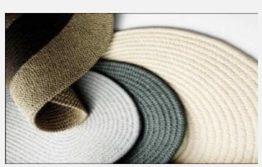
CURRENT AREAS OF USE

Packaging – Fornitures – Agricolture – Bags – Personal care

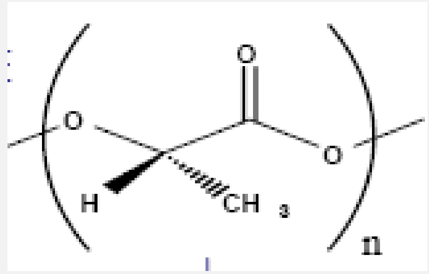
Short term use



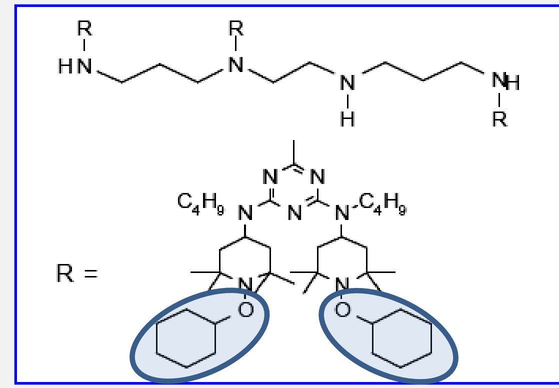
Durable applications
(automotive – textile – E&E)

Materials

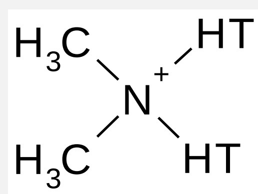
PLA 3051D

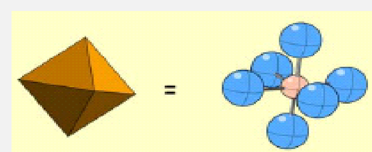


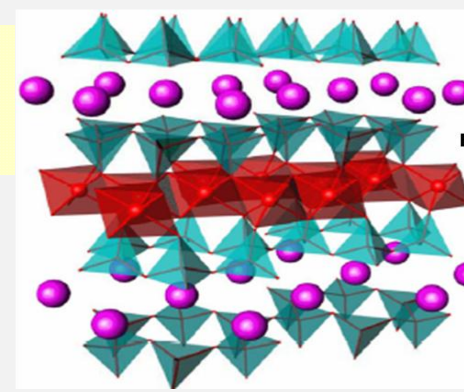
Flame retardant: Flame Stab NOR 116 (FI)



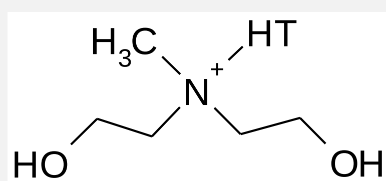
- Cloisite 20A (Cl20A)

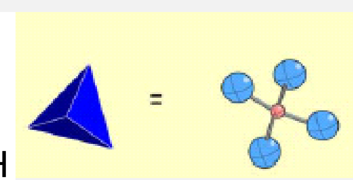






- Cloisite 30B (Cl30B)



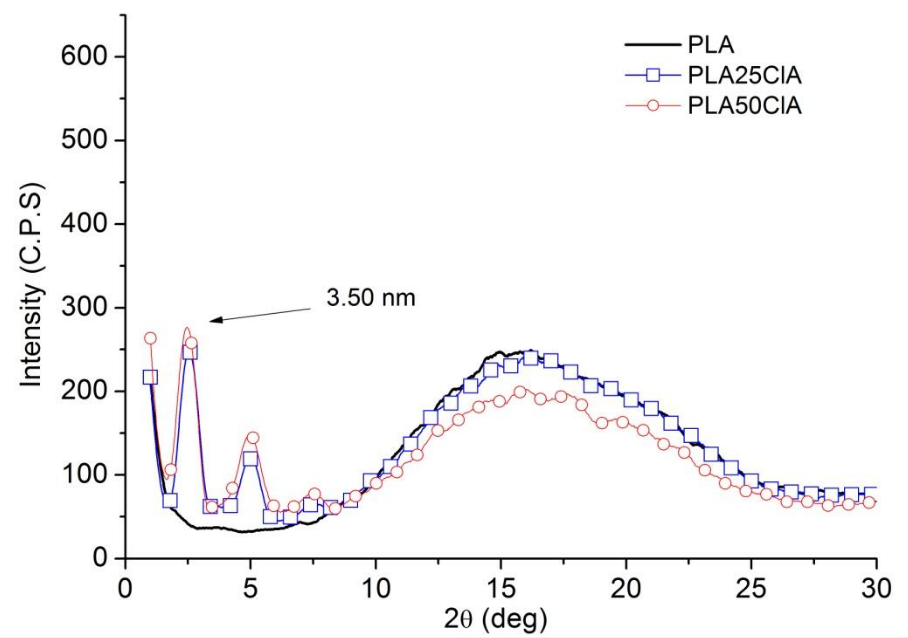


Sample preparation

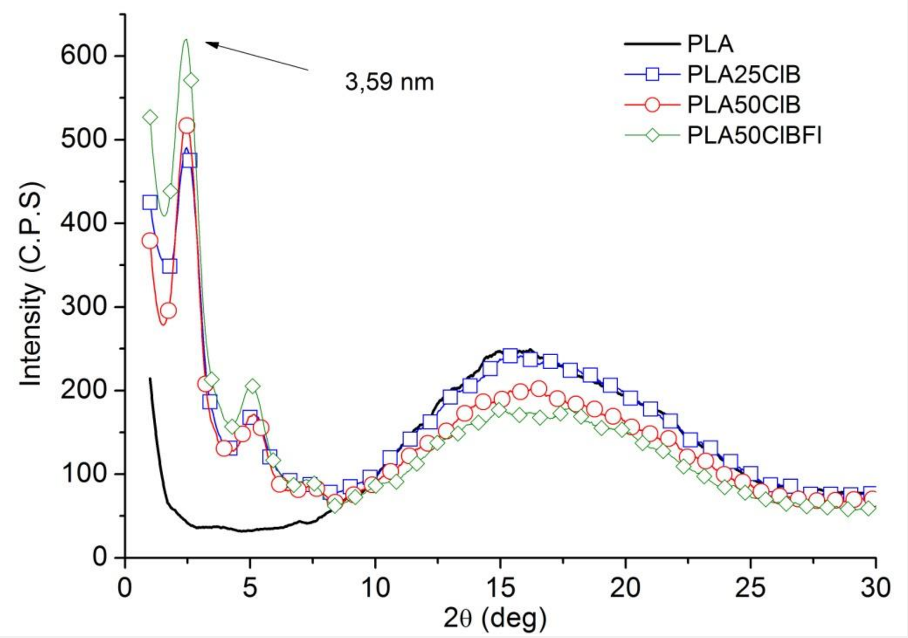
Sample	PLA	Nanofiller	Fl
	%	%(Type)	%
PLA	100.0	-	-
PLAFl	99.0	-	1.0
PLA25ClA	97.5	2.5 (Cl20A)	-
PLA50ClA	95.0	5.0 (Cl20A)	-
PLA25ClB	97.5	2.5 (Cl30B)	-
PLA50ClB	95.0	5.0 (Cl30B)	-
PLA50ClBFl	94.0	5.0 (Cl30B)	1.0

Melt-processing Leistritz co-rotating twin screw extruder (d=18 mm, l/d=40). Flow 4.0 kg/h, speed 150 rpm

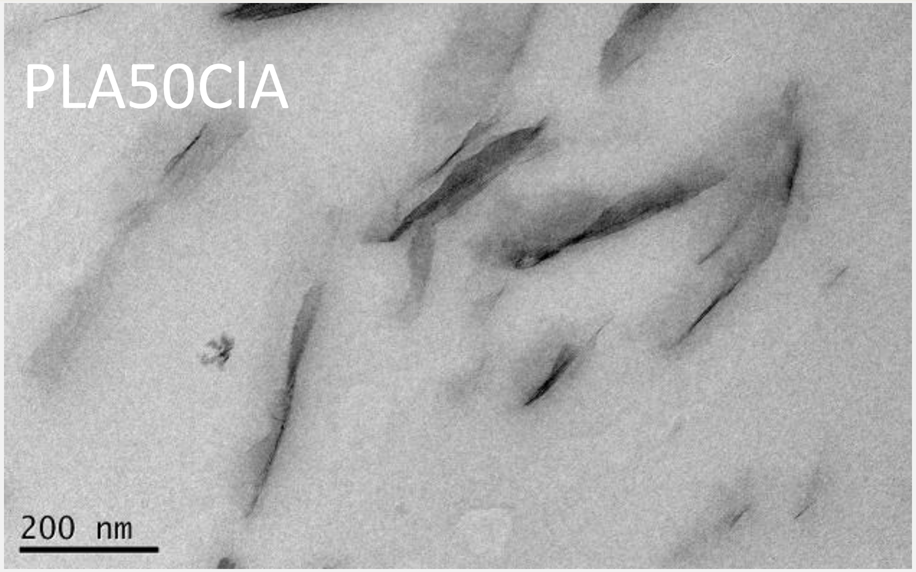
MORPHOLOGY (XRD analyses)

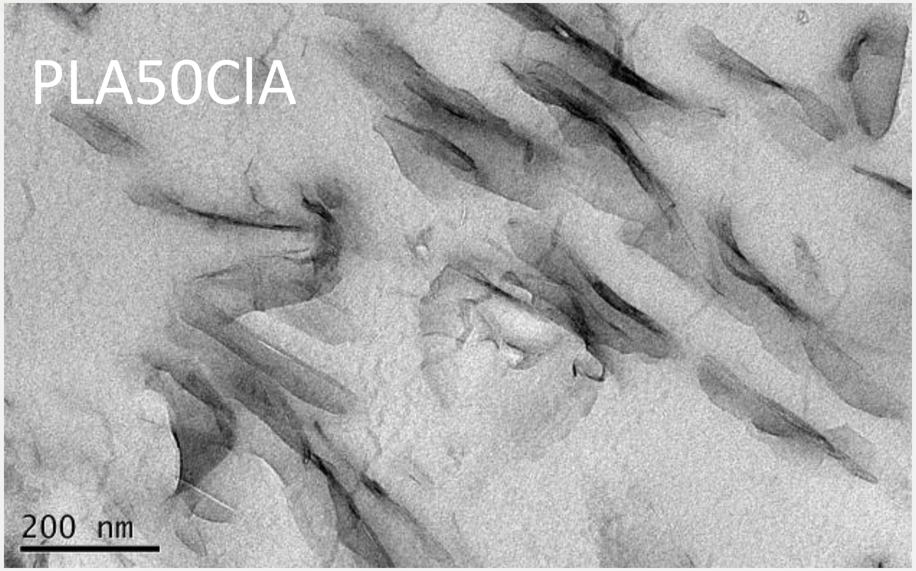


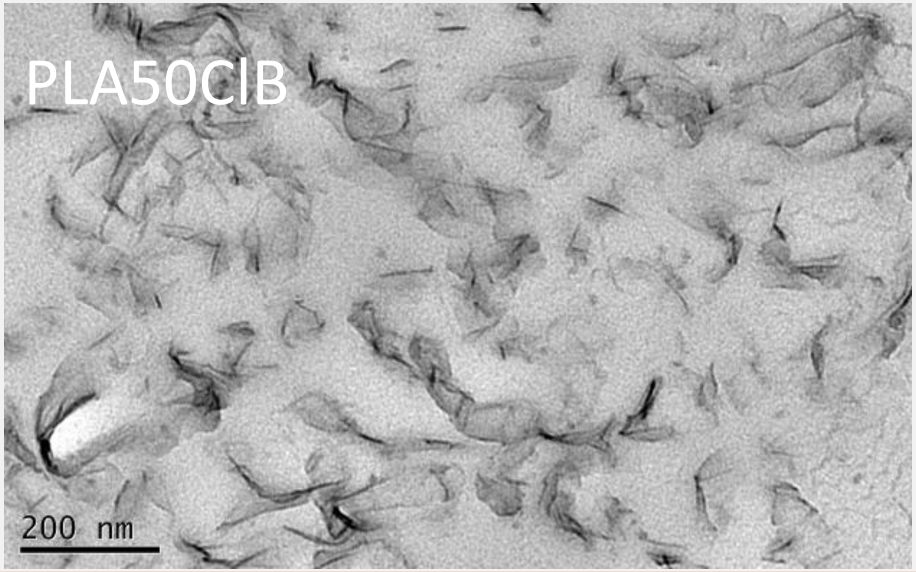
From X-ray analyses intercalated structure is foreseen

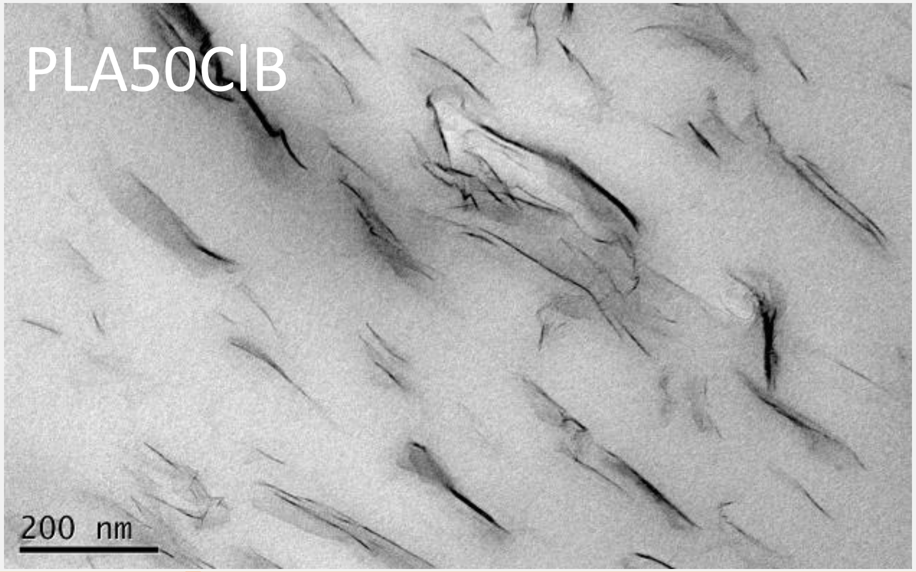


MORPHOLOGY (TEM)

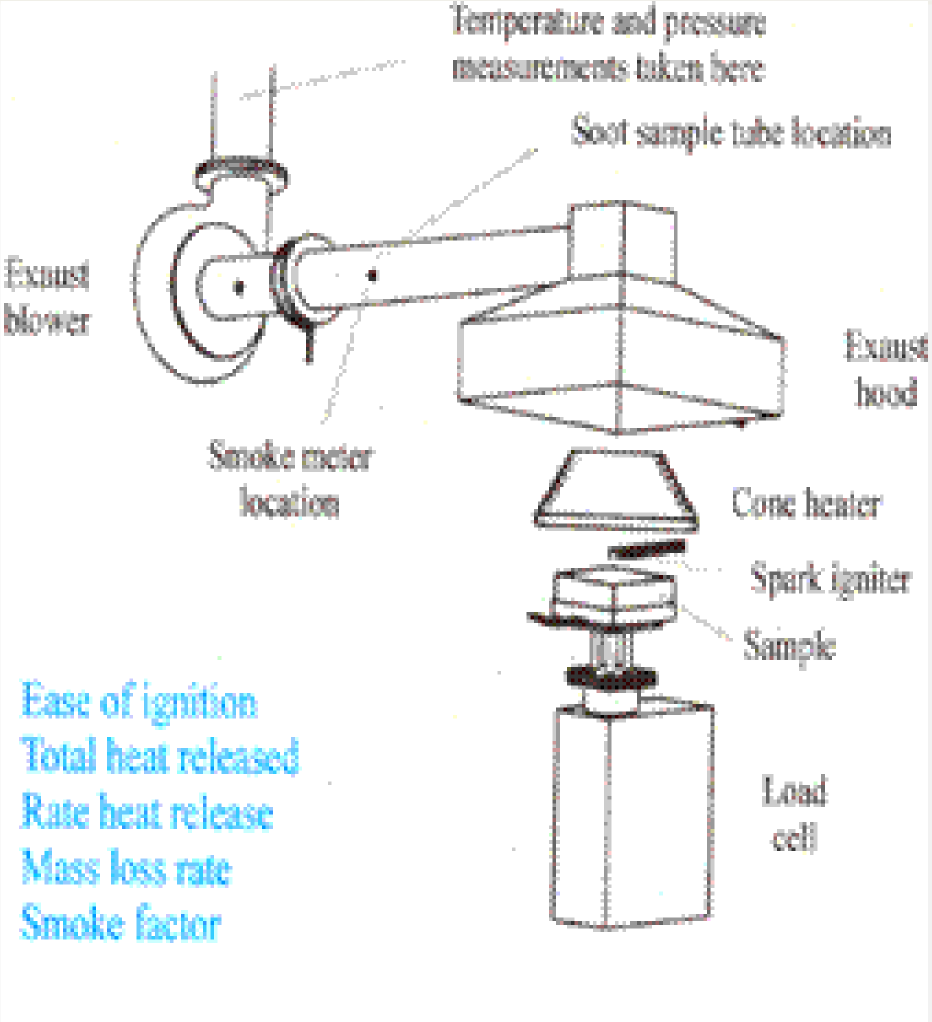








Cone calorimeter



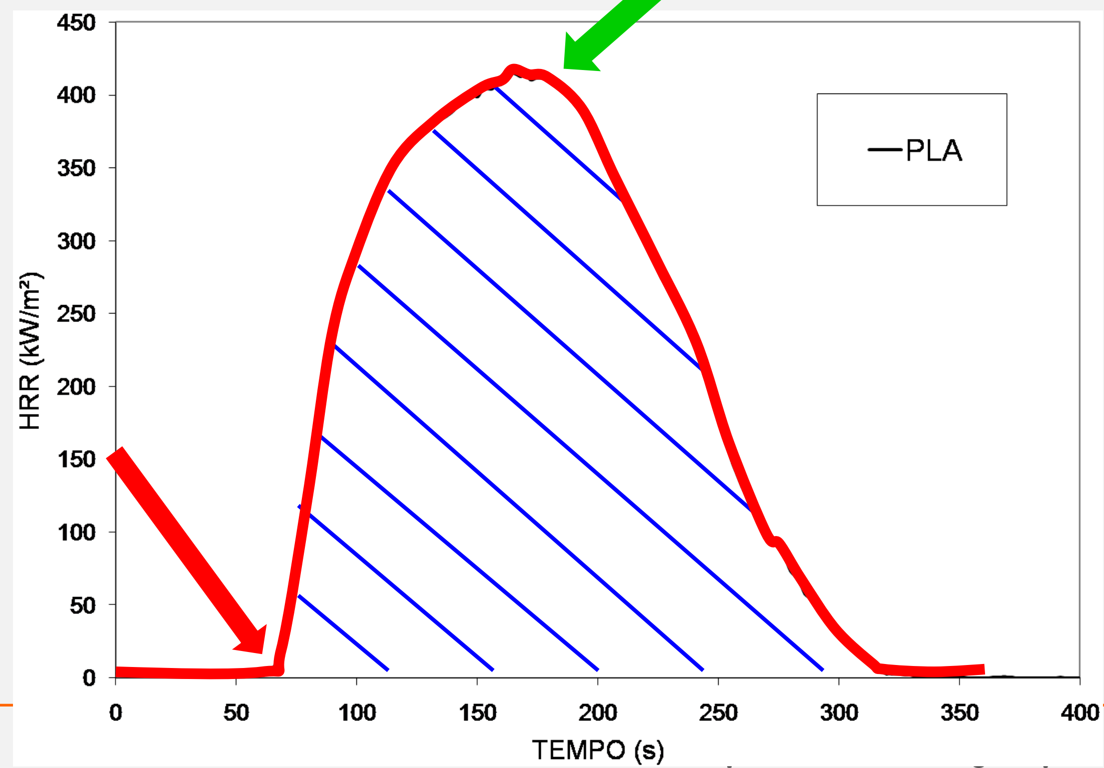
General view of Cone Calorimeter

Cone calorimeter

Forced combustion: irradited power 35 KW/m^2

PARAMETRI VALUTATI:

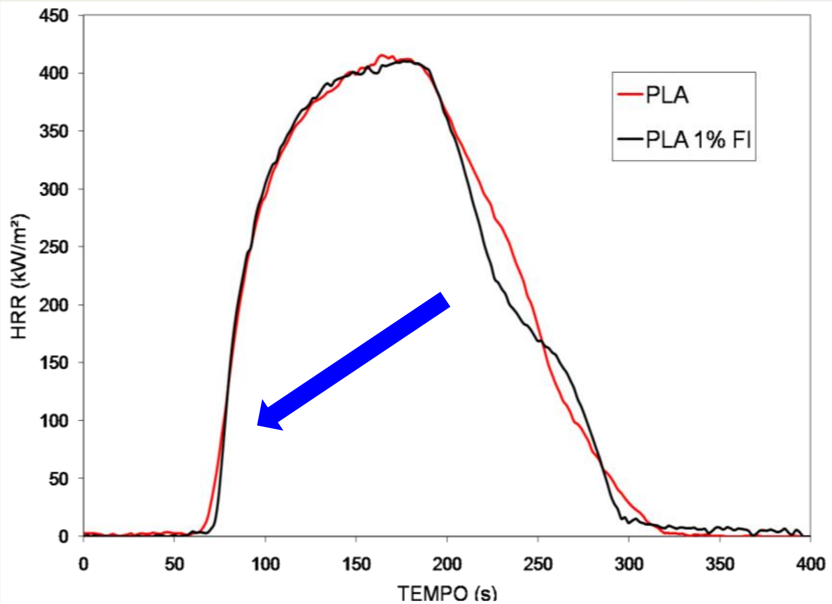
- Heat Release Rate (HRR) vs time
- Time To Ignition (TTI)
- Peak Heat Release Rate (pkHRR)
- Total Heat Release (THR)

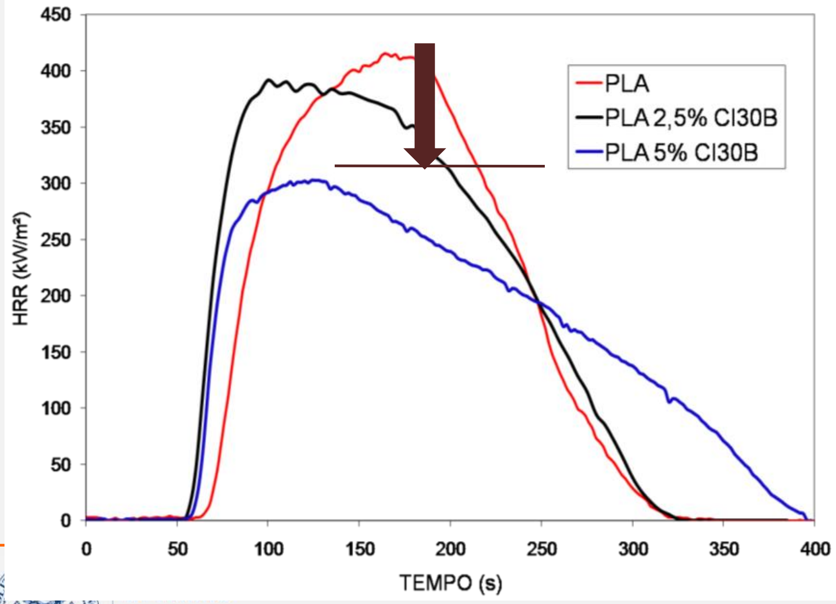


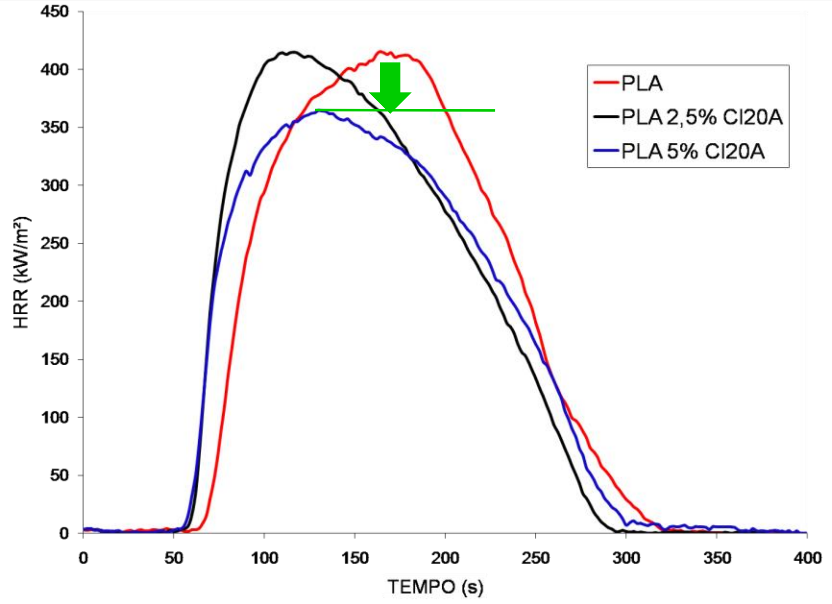
Aim

- Decrease of released heat
- Delay of TTI

Heat Release rate curves



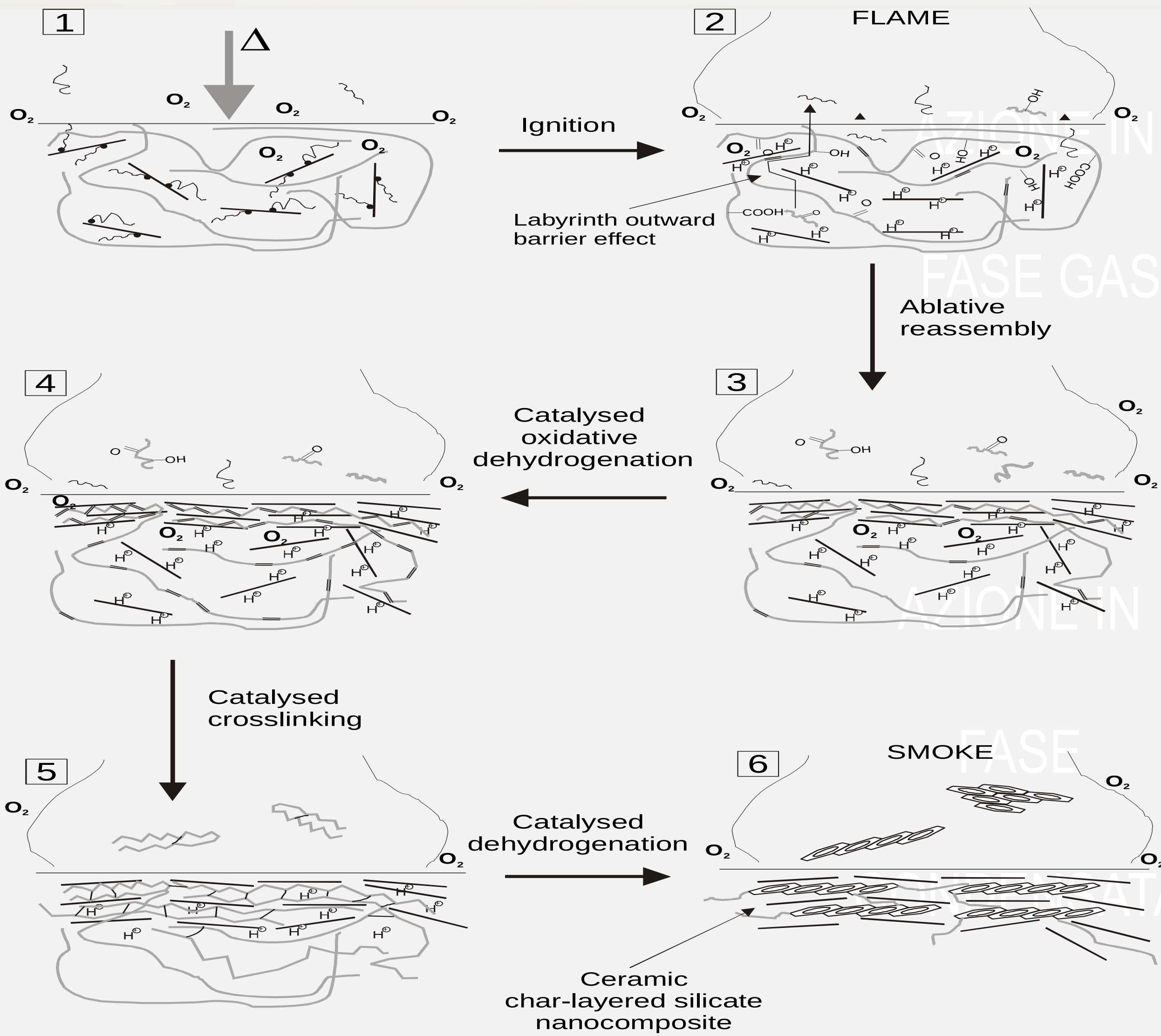




Cone calorimeter data

Sample	TTI	pHRR	THR
	(s)	(MW/m^2)	(MJ/m^2)
PLA	67	415	63
PLAFl	71	410	62
PLA25ClA	59	415	61
PLA50ClA	60	364	60
PLA25ClB	57	392	67
PLA50ClB	59	303	62
PLA50ClBFl	45	306	66

G. Camino,T. Kashiwagi, L. Falqui et al.
"Cone Calorimeter Combustion and Gasification Studies of Polymer Layered Silicate Nanocomposites" Chemistry of Material, 14(2), 881-887, (2002).



Decrease of HRR and pHRR

pHRR = 415 MW/m^2

PLA

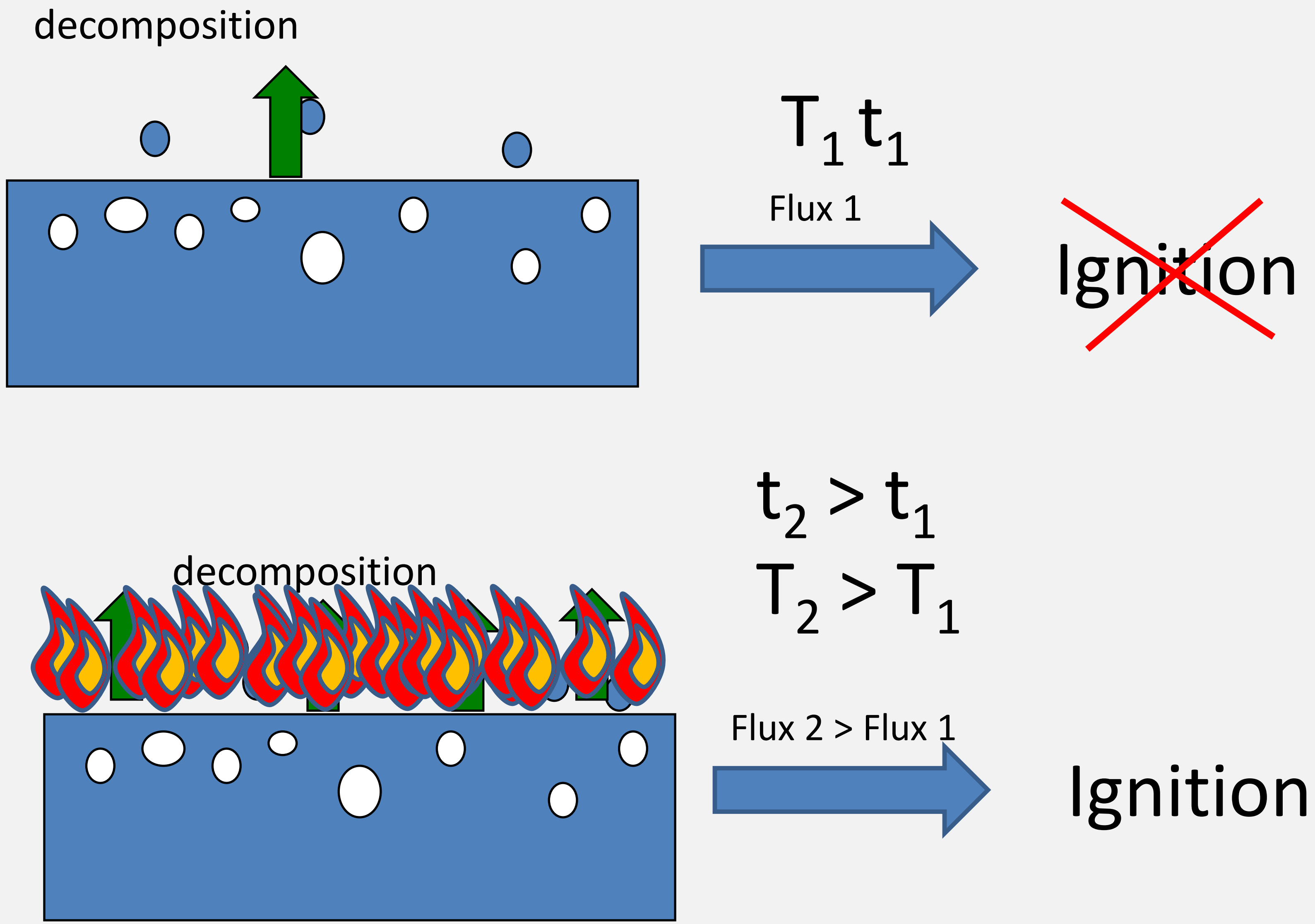
pHRR = 415 MW/m^2

PLA25ClB

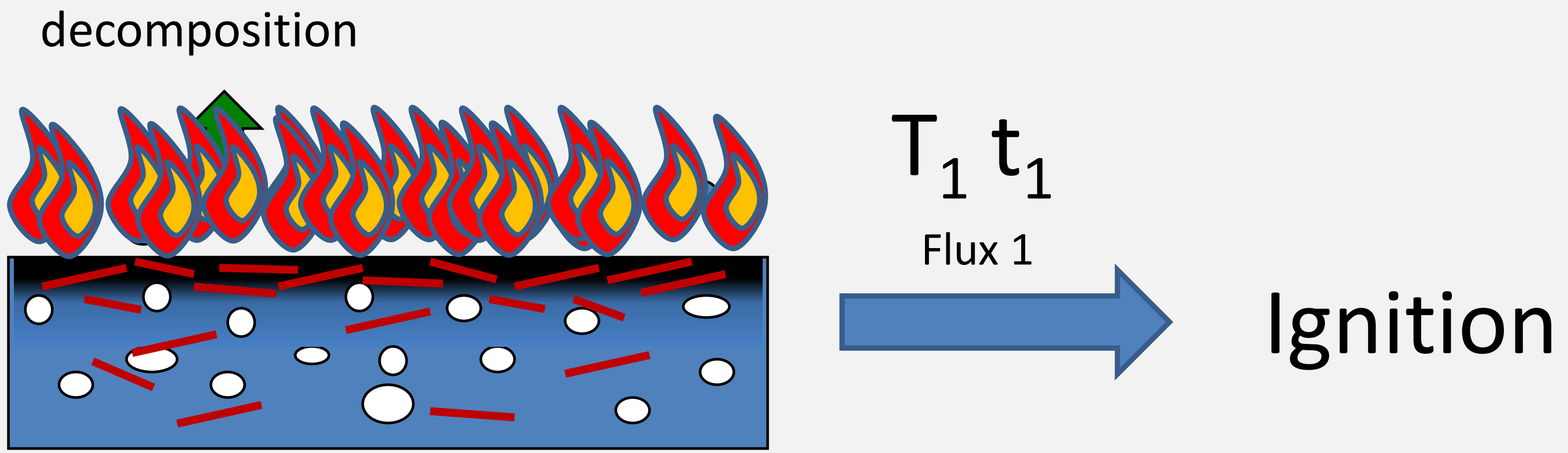
pHRR = 300 MW/m^2

PLA50ClB

Time to ignition of polymer



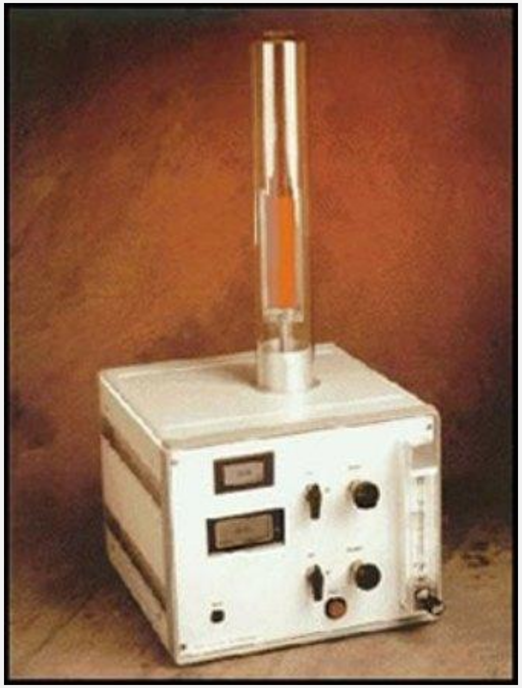
Time to ignition of polymer nanocomposites



nanoparticle-catalyzed oxidation of the gases generated at the surface of the condensed phase by volatilization of the polymer*

* Fina A, Camino G. Ignition mechanisms in polymers and polymer nanocomposites (2011) Polym. Adv. Technol. 22(7): 1147-1155.

LIMITING OXYGEN INDEX (LOI)



Limiting oxygen index (LOI) the minimum oxygen concentration necessary to just support flaming combustion of the material

OI= Oxygen index

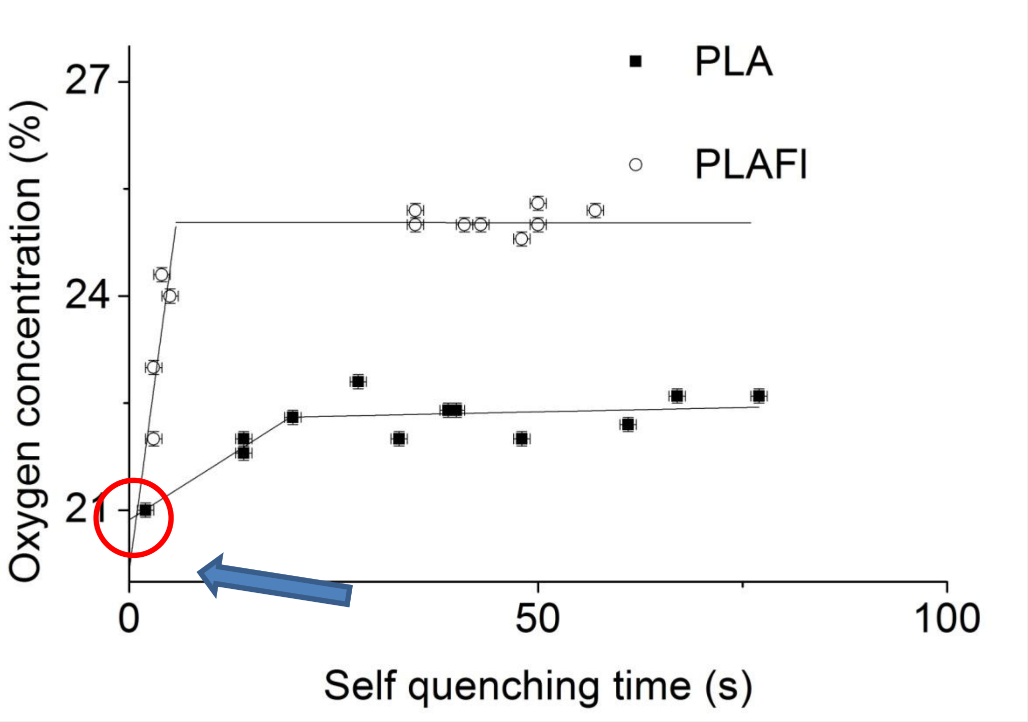
Sample	OI (%)
PLA	23.2±0.1
PLAFl	25.3±0.1
PLA25ClA	21.6±0.1
PLA50ClA	23.2±0.1
PLA25ClB	19.3±0.1
PLA50ClB	21.5±0.1
PLA50ClBFl	21.8±0.1

Self quenching time (SQT)

"Self-Quenching Time"(SQT) the time necessary to extinct the flame

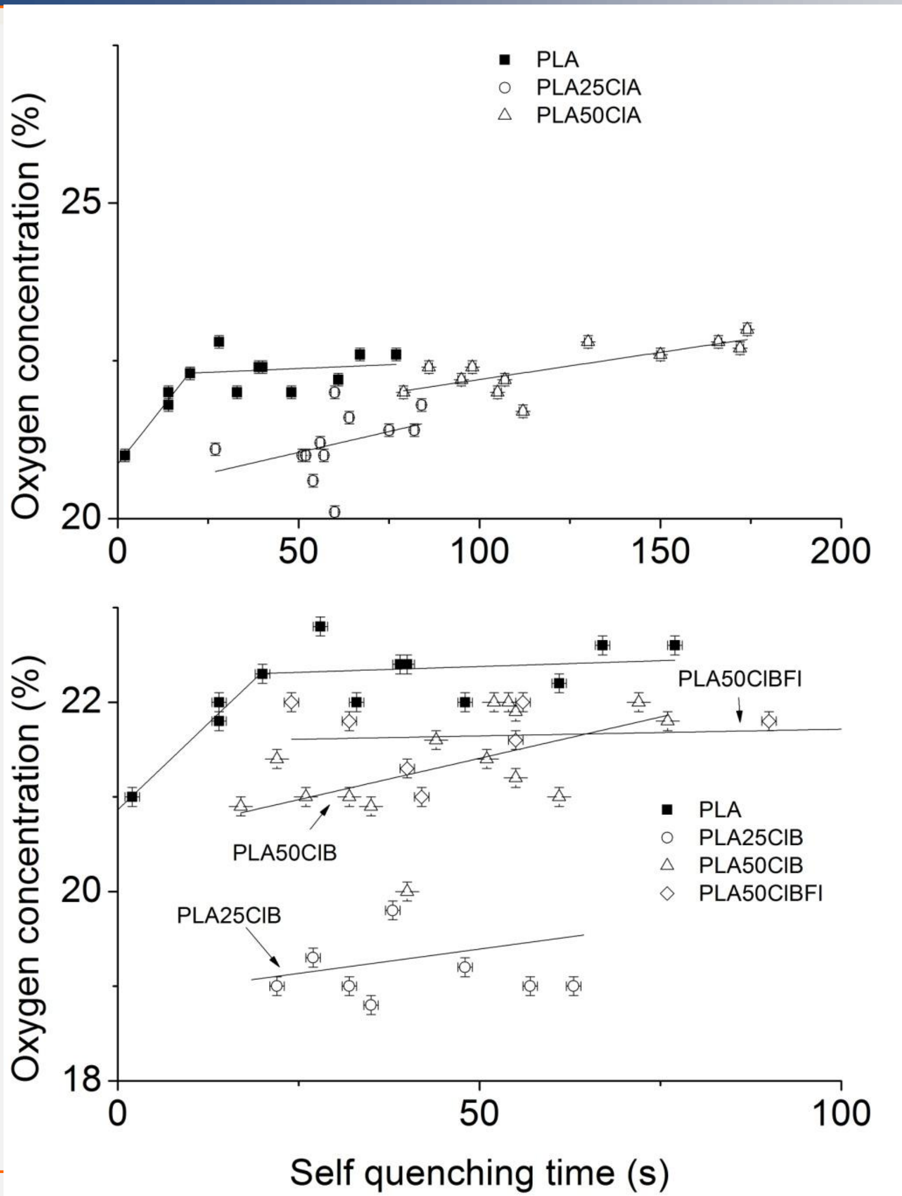
1st Region "Unstable burning"

2nd Region "Stable burning"



IOI=ignition oxygen index

Self quenching time of nanocomposites



Sample	OI (%)	IOI (%)
PLA	23.2±0.1	20.9±0.1
PLAFl	25.3±0.1	20.9±0.1
PLA25ClA	21.6±0.1	20.4±0.6
PLA50ClA	23.2±0.1	21.3±0.3
PLA25ClB	19.3±0.1	19.2±0.2
PLA50ClB	21.5±0.1	20.5±0.4
PLA50ClBFl	21.8±0.1	21.6±0.2

The IOI is quite similar for all the materials

It is impossible to recognize the two different regions, once the nanocomposite ignites the flame is stable

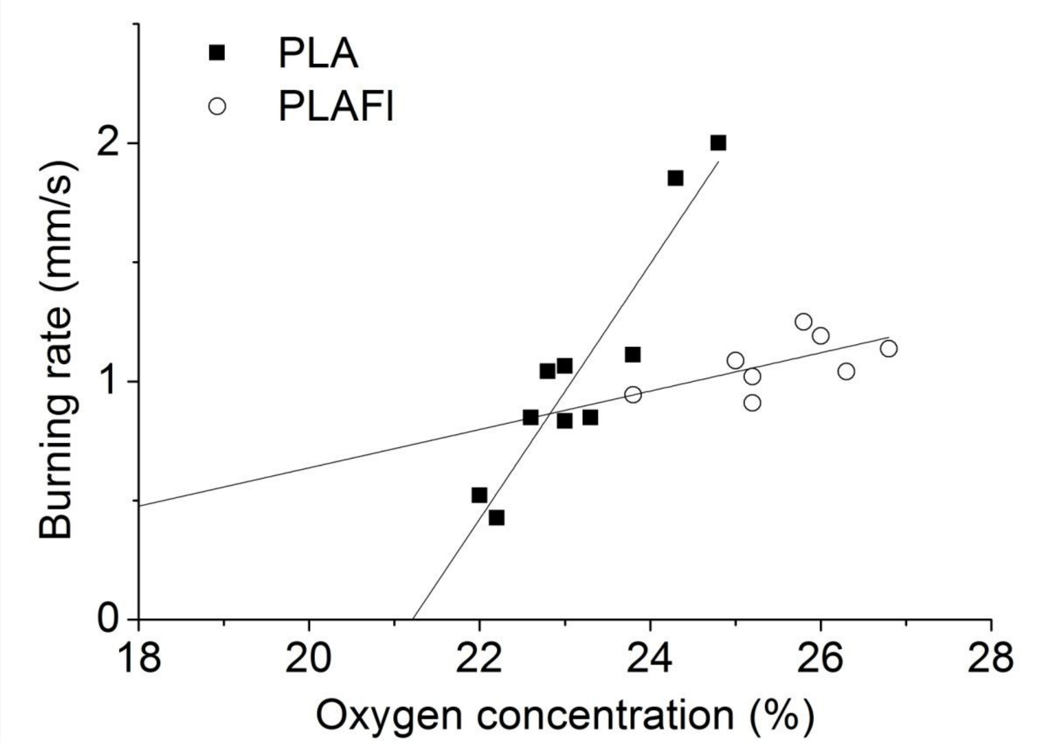
Once a nanocomposite ignite difficultly it stops burning

In nanocomposites ignition is controlled by nanoparticle-catalyzed oxidation of the gases generated at the surface of the condensed phase by volatilization of the polymer*

Conditions for ignition are thus created as soon as the polymer decomposition temperature is reached

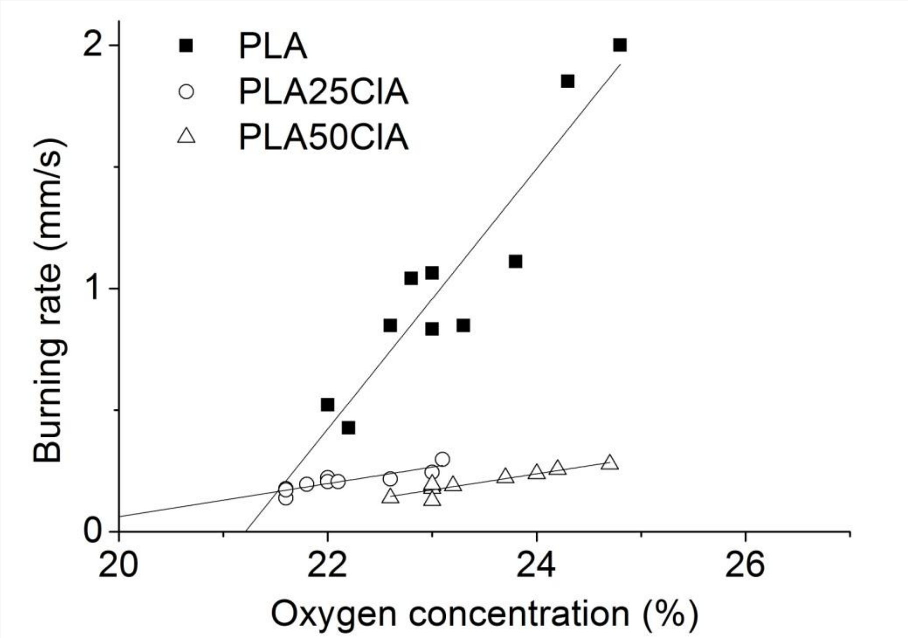
* Fina A, Camino G. Ignition mechanisms in polymers and polymer nanocomposites (2011) Polym. Adv. Technol. 22(7): 1147-1155

Burning rate (BR)



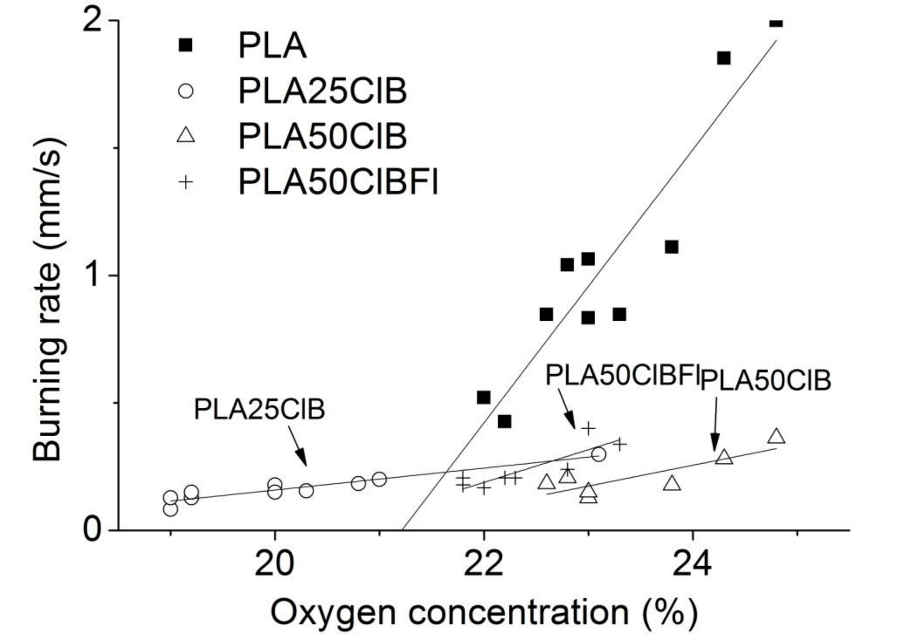
$$\frac{\Delta l}{\text{time}} = \text{Burning rate (BR)}$$

Burning rate of nanocomposites



The BR of nanocomposites at the same OC could be from 10 to 20 times lower that pure PLA

The effect of clay on the BR is directly related to the quantity of clay present in the nanocomposite



Burning rate of nanocomposites (BR)

Sample	ΔBR/ΔOC
PLA	0.54±0.07
PLAFl	0.08±0.04
PLA25ClA	0.07±0.01
PLA50ClA	0.07±0.01
PLA25ClB	0.04±0.01
PLA50ClB	0.08±0.02
PLA50ClBFl	0.13±0.03

The lines are practically flat

No more dipendent from the oxygen concentration

Mass transport problems

Glass-forming materials

Intumescent with char-forming systems is one of the most effective means of restrict the flow of heat and/or oxygen.

Many times , char formation may not be sufficient. Char which lacks structural integrity and/or thermal stability will provideonly minimal benefit in a fully developed fire scenario. Related to char stability is the phenomenon of afterglow i.e., char oxidation

Solution could be the use of low melting glasses

Glasses can be formed from a wide number of inorganic salt (sulfates, carbonates, phospates etc…) and in the right proportion it is possible to achieve different temperatures on the basis of the specific polymer

Ammonium pentaborate $(NH_4)_2B_{10}O_{16}$

Inorganic-based

Non-halogenated

Intumescent

Glass forming

Compostable ?

$$(NH_4)_2B_{10}O_{16} \cdot 8H10 \rightarrow 5B_2O_3 + 2NH_3 + 9\ H_2O$$

The pentaborate undergoes relatively low temperature thermal decomposition accompanied by in situ glass formation

(1) Myers, R. E. Dickens, E. D. Licursi, E.; Evans, R. E. *Journal of Fire Sciences*. **1985**, *3*, 432-44

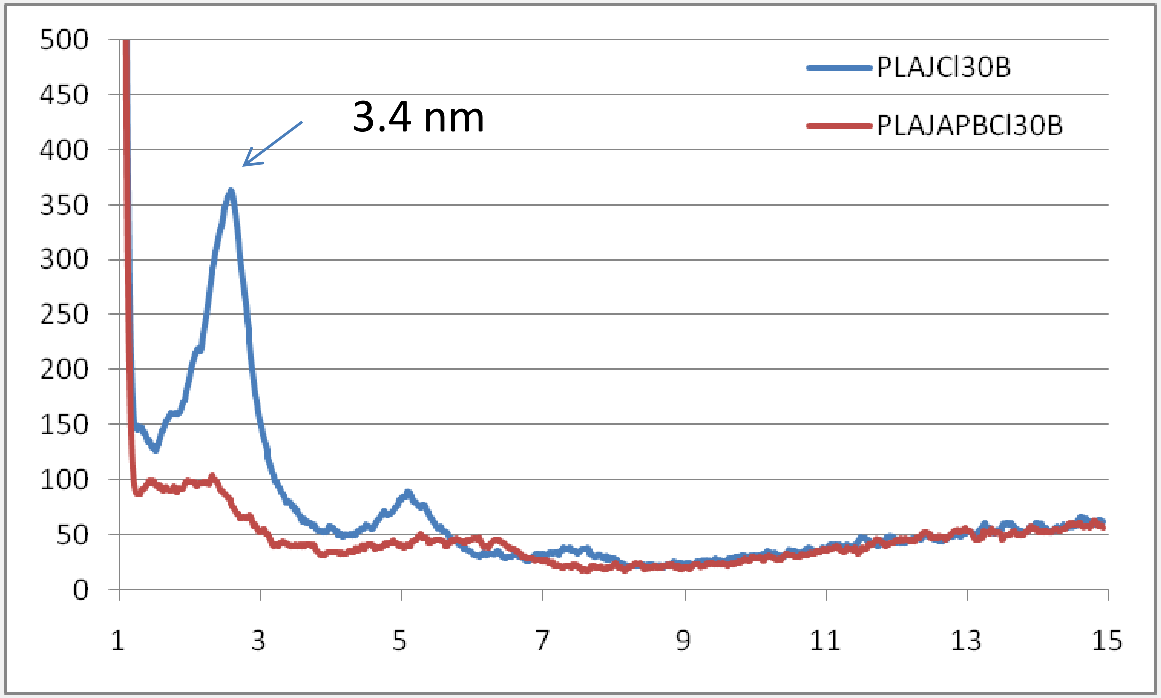
(2) Myers, R. E.; Licursi, E. *Journal of Fire Sciences*. **1985**, *3*, 415-431.

Sample preparation

Sample	Joncryl	Nanofiller	APB
	%	%	%
PLAJ	1.0	-	-
PLAJ Cl30B	1.0	5.0	-
PLAJAPB	1.0	-	10
PLAJAPBCl30B	1.0	5.0	10

Melt-processing Leistritz co-rotating twin screw extruder (d=18 mm, l/d=40). Flow 4.0 kg/h, speed 150 rpm

MORPHOLOGY (XRD analyses)

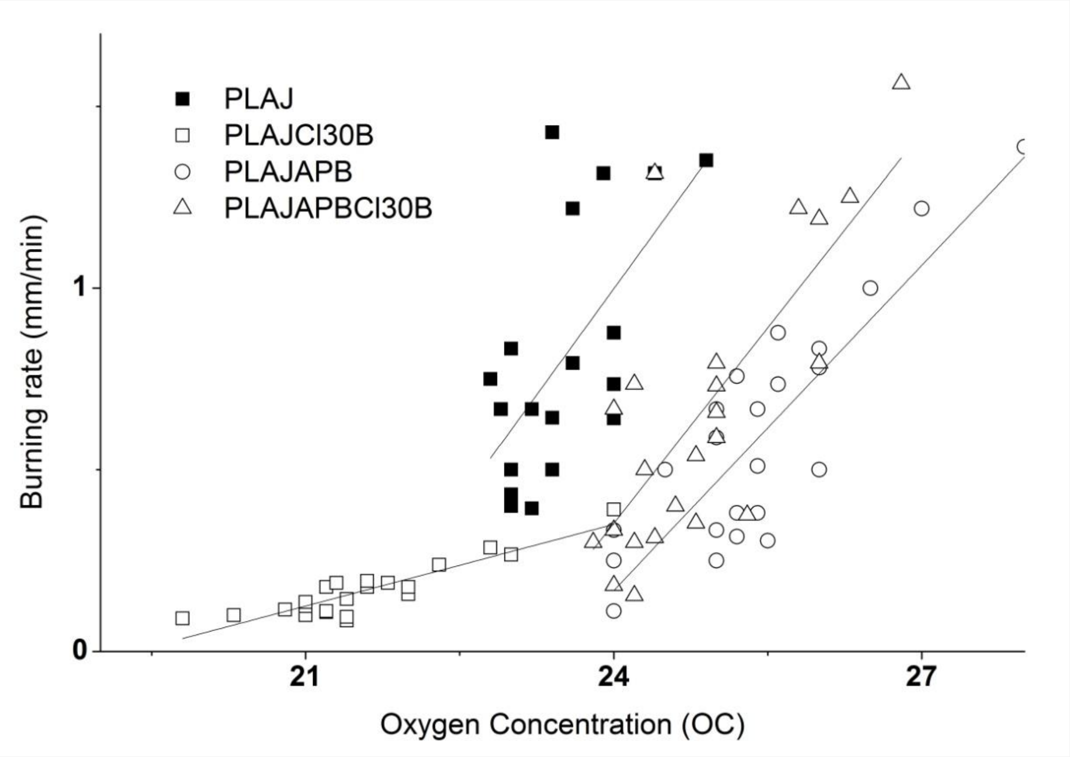


LIMITING OXYGEN INDEX (LOI)

Sample	OI (%)
PLAJ	23.4±0.1
PLAJCl30B	21.6±0.1
PLAJAPB	25.5±0.1
PLAJAPBCl30B	24.5±0.1

LOI increased in presence of APB, also in this case the presence of montmorillonite decreases the Oxigen Index of the composites

Burning rate of nanocomposites



Sample	ΔBR/ΔOC
PLAJ	0.39±0.11
PLAJCl30B	0.07±0.01
PLAJAPB	0.30±0.04
PLAJAPBCl30B	0.36±0.07

The BR of nanocomposite depends also from the other components