FIRE RETARDANT BEHAVIOUR OF POLYLACTIC ACID NANOCOMPOSITES

W. Ping[1], S. Bocchini[2], A. Di Blasio[2], G. Camino[2]

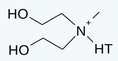
[1] *School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai, People's Republic of China*

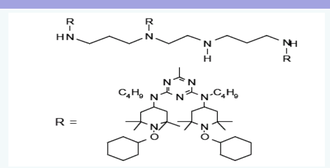
[2] *Polytechnic of Turin, Alessandria site, Italy*

First applications of PLA were designed for disposable materials (e.g. packaging) or semi-durable materials (e.g. textile) where flame retardancy is not required. However because of increase of PLA for durable application, the fire retardancy issue is becoming important and it is expected that in the next future more and more scientific paper will be devoted to the subject. Actually most of the work done on PLA is on the use of traditional fire retardants developed for other polymers especially traditional polyesters such as PET or other polymers such as polycarbonate. The use of clay could help in the development of fire retardant plastics based on biopolyesters. The main goal of this work is to study clay nanocomposites during heating and the derived thermal and fire behavior.

Materials

The Poly(lactic acid), 3051D- (PLA) was supplied by Nature Works (USA). Flamestab NOR 116 a flame retardant and flame retardant synergist in polyolefin applications was supplied by Ciba specialty chemical The nanofillers and flame retardant used are listed in Table below:

Filler (Name)	Organic modifier	Filler type
Cloisite 20A(Cl)		Montmorillonite
Closite 30B (Cl30B)		Montmorillonite

Sample	Formula
Flamestab NOR 116 (Fl)	

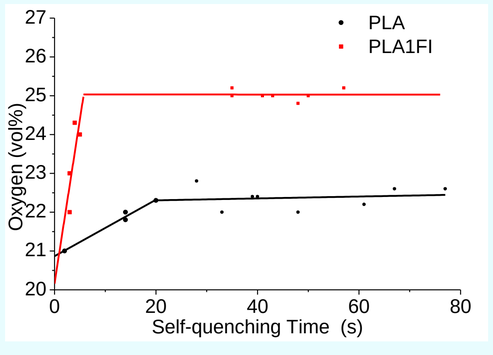
Material processing

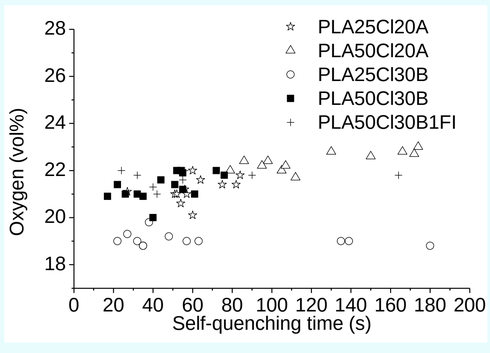
The composites were prepared via melt-processing using a leistritz co-rotating twin screw extruder (d=18 mm, l/d=40). Flow with 4.0 kg/h, speed with 150 rpm were used. The residence time was about 50s.The samples were prepared by direct addition of the different nanofillers. Composition were listed below:

Sample	PLA	Flamestab NOR 116 (Fl)	Filler	
	%wt	%wt	Type	%wt
PLA	100.0	-	-	-
PLA1Fl	99.0	1.0	-	-
PLA25Cl	97.5	-	Cl20A	2.5
PLA50Cl	95.0	-	Cl20A	5.0
PLA25Cl30B	97.5	-	Cl30B	2.5
PLA50Cl30B	95.0	-	Cl30B	5.0
PLA50Cl30BFl	94.0	1.0	Cl30B	5.0

Limiting oxygen index (Self quenching time)

For a more detailed evaluation of fire behaviour not only the limiting oxygen index number (LOI) is reported but also the burning time as a function of oxygen concentration (OC)*. The time interval between the removal of the ignition flame and the extinction of the burning specimen named "Self-Quenching Time"(SQT), is reported as a function of the oxygen concentration. The plots of PLA and PLAFl can be separated into two successive approximately linear regions which is the behaviour most often found for polymer materials. In the first region a large increase in oxygen concentration is required to increase the self quenching time. The interval between the first and the second region is the change from an unstable to stable burning. In this case Fl works as a flame retardant because it increases of about 3 %vol the oxygen concentration in order to have a stable burning. Upon addition of nanoclays, the oxygen concentration at which PLA ignition by the external flame just becomes possible, also ensures self-sustained combustion to occur, with suppression of the unstable combustion regime observed with virgin PLA, in other words, the oxygen index at which nanocomposites ignites and their LOI are coincident. This generally results in a lower LOI value for nanocomposites as compared to PLA, apart from PLA50CL20A which LOI is comparable to PLA





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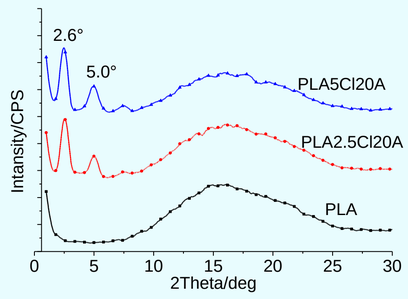
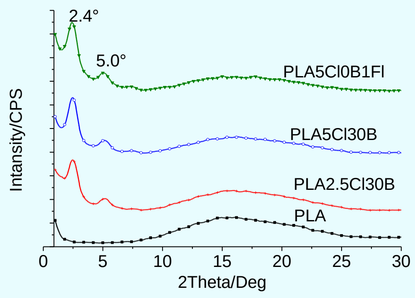
Morphology

As a result of PLA melt blending with 2.5 and 5.0 wt% of (organo-modified) montmorillonite, intercalated nanocomposites were prepared by using Cloisite 20A or Cloisite 30B. There is no major modification between 2.5 wt% and 5 wt% for both clays. PLA is characterized by a broad intensity with maximum approximately at 2θ=17°, indicating an amorphous structure for this sample. The interlayer spacing (d_{001}) diffraction angle obtained by XRD measurements for Cl20A is equal to 2θ= 3.6°, when adding Cl20A to the PLA, , for both PLACl20A nanocomposites a sharp peak is observed at 2θ=2.6°, equivalent to a d_{001}= 3.4 nm with an increase of the interlayer distance of 1 nm compared with pure Cl20A, .This increase is accompanied by the appearance of a small peak at 5° due to the d_{002} of the dispersed Cl20A.

In the case of the system of Cl30B with PLA based nanocomposites, a sharp peak shift to 2θ=2.4°, which phenomena is similar to systems of PLA Cl20A, but the d_{001} increases to 3.7 nm from 1.8 nm of the original Cl30B organoclay, interlayer distance.

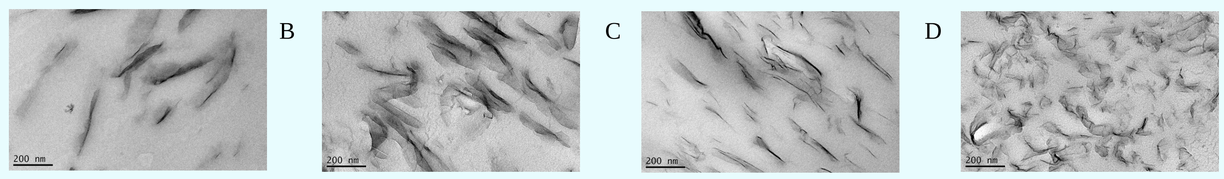




Sample	Interlayer distance d_{001}	
	2θ	nm
Cl	3.60	2.4
Cl30B	5.00	1.8
PLA25Cl	2.60	3.4
PLA50Cl	2.60	3.4
PLA25Cl30B	2.43	3.7
PLA50Cl30B	2.43	3.7
PLA50Cl30BFl	2.43	3.7

TEM analyses

PLA based nanocomposites were further analyzed by TEM. The incorporation of Cl20A in the PLA matrix shows certain level of intercalation as well as the occurrence of exfoliated silicate layers. When correlating these observations with XRD results, we can conclude that the Cl20A forms partially exfoliated nanocomposites. The same results were obtained with Cl30B based nanocomposites. There is a certain level of intercalation but the numbers of silicate layers for stack are lower respect to Cl20A and higher numbers of small stacks of swollen clay layers and single dispersed layers can be observed in the TEM micrograph .From XRD and TEM results, it is clear that the dispersion and interaction of the Cl30B in PLA is better than that obtained with Cl20A. This can be attributed to the stronger interactions between the polymers and Cl 30B, originated from the hydrogen bonding between the carbonyl group of PLA and the hydroxyl groups.

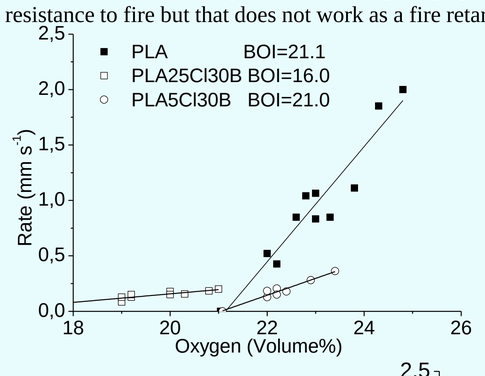


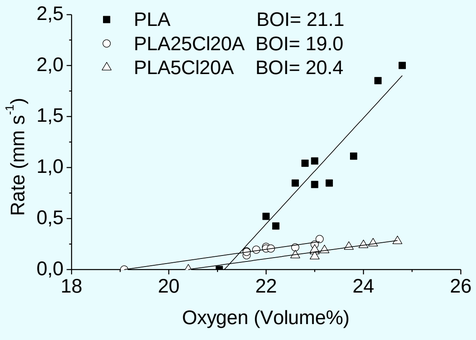
TEM analyses of different nanocomposites A) B) PLA50Cl20A C) D) PLA50Cl30B

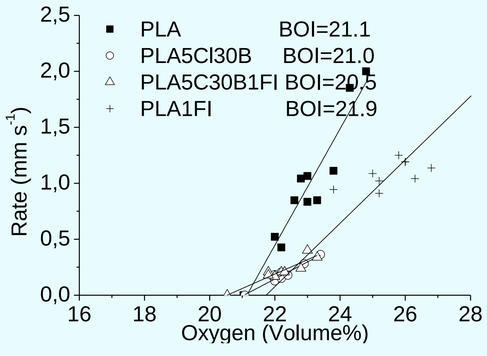
Limiting oxygen index (Burning rate)

Burning rate as a function of oxygen concentration is easily measured in the oxygen index test apparatus by measuring the spreading time of the flame between two marks at a known distance on the specimen. A Burning Oxygen Index (BOI)* can also be obtained by extrapolating BR to BR=0, which meaning is indeed similar to that of oxygen index at which the sample ignites (OC below which ignition does not occur) since it gives the OC below which burning would not occur.

The plots shows that the nanocomposites have a BOI lower that PLA alone, as expected the BOI of the different nanocomposites are directly linked to the concentration of the different nanoparticles and their dispersion, thus it is possible to have a quantitative correlation between filler type, concentration and dispersion and the BOI of the different nanocomposites. Moreover in these graphs the effect of nanoclay on fire retardacy is clearly exposed: the different nanocomposites burns at lower oxygen index but the conbustion rate is usually lower that the pure polymer thus the different clays could be considered as an additive that improves the resistance to fire but that does not work as a fire retardant if used alone.







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