



Polo di innovazione tessile

17° Innovation Day «Tessili e Materiali Compositi»

29 Ottobre 2014

# Compositi termoplastici di tipo commingled a matrice nanocomposita

**Marco Monti**

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## Introduzione

Il presente lavoro fa parte di un più ampio studio su compositi strutturali dalle migliorate proprietà di risposta al fuoco.

Il progetto è stato cofinanziato dalla Comunità Europea nell'ambito del 7° Programma Quadro, grant agreement n° 246037, Progetto FIRE-RESIST.

Nello specifico, il presente lavoro è frutto di una collaborazione di Proplast con:



[www.fire-resist.eu](http://www.fire-resist.eu)



*SP Technical Research  
Institute of Sweden  
Borås, Sweden*

swerea | SICOMP

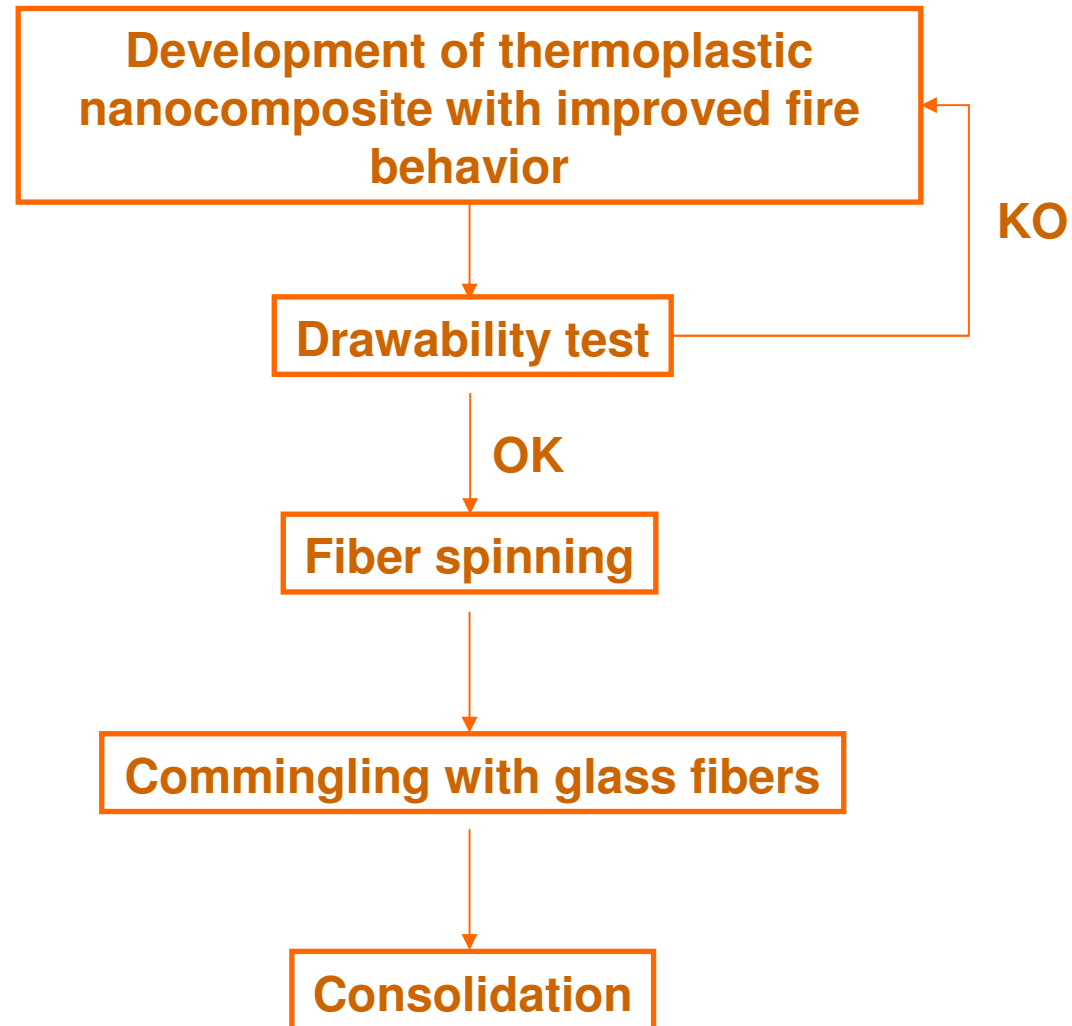
*Swerea SICOMP  
Piteå, Sweden*



*Politecnico di Torino  
Sede di Alessandria (AL)*



- L'aggiunta di una nanocarica ad una matrice polimerica può portare al miglioramento delle prestazioni od anche all'ottenimento di proprietà completamente nuove.
- Il commingling è una delle tecniche promettenti per la produzione di compositi termoplastici fibrorinforzati.
- Rispetto all'aggiunta di nanocariche in altri sistemi compositi (es. matrici termoindurenti), in questo caso si evitano problemi legati alla presenza delle fibre (es. filtrazione, ecc)
- In questo lavoro un nanocomposito PA6-nanoargilla è stato filato e unito a fibre vetro per la formazione di un composito consolidato.





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# Development of a nanocomposite with improved fire behavior

## MATRIX

**PA6** Ultramid B27 (BASF)

## NANOFILLER

**Category:** natural montmorillonite (layered silicate) modified with a quaternary ammonium salt.

**Tradename:** Cloisite 30B (Rockwood Additives)

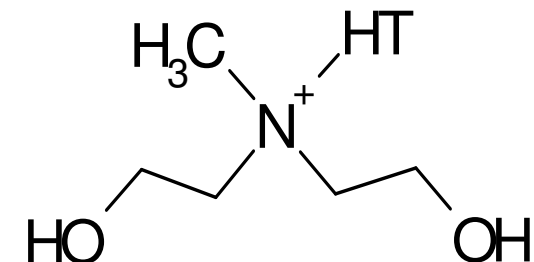
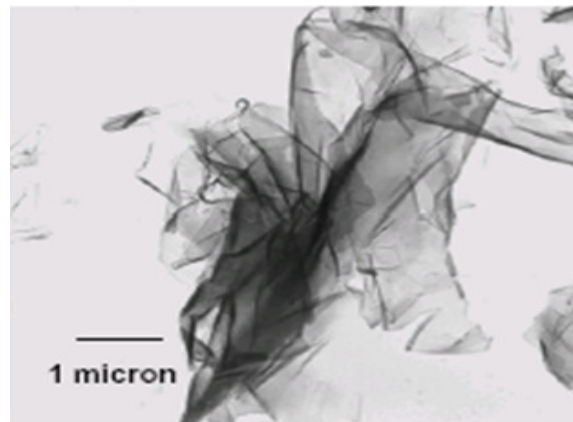
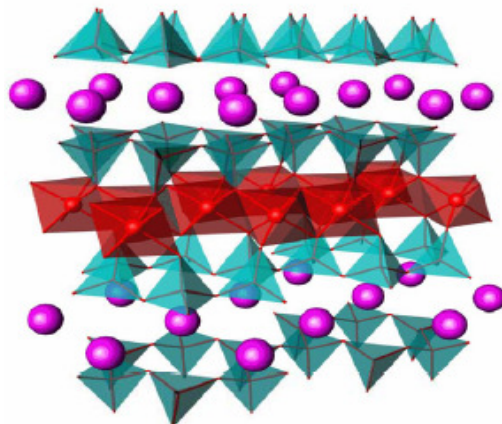
**Weight fraction:** 2 and 4wt%

### Product description

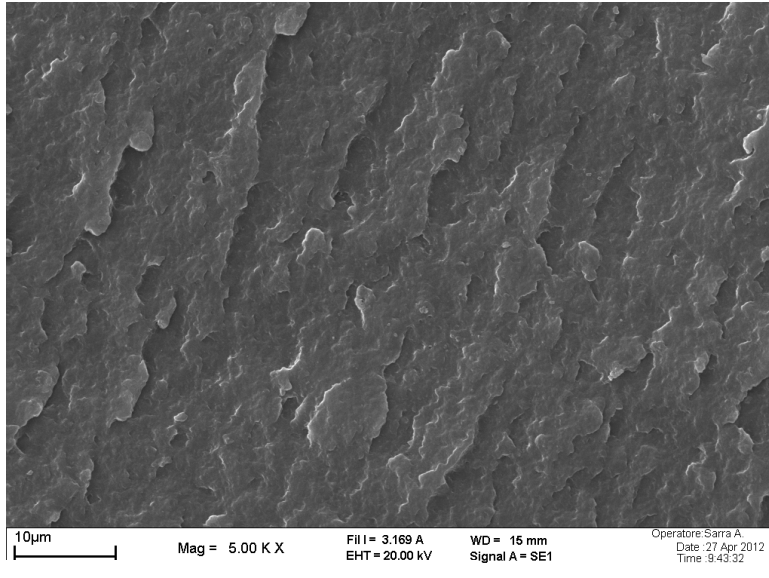
Ultramid® B27 03 is a polyamide 6 for the production of bright textile and carpet fibers.

### Specification

Specification	Test method	Unit	Value
Relative Viscosity (RV) 1% [m/v] in 96% [m/m] sulfuric acid	According to ISO 307		2.67 - 2.73
Viscosity Number (VN) 0,5% [m/v] in 96% [m/m] sulfuric acid	According to ISO 307 (calculated by Huggins method)	ml/g	146 - 151
Moisture content	According to ISO 15512	% [m/m]	max. 0.06
Extractables	According to ISO 6427- chips not ground/16h	% [m/m]	max. 0.6

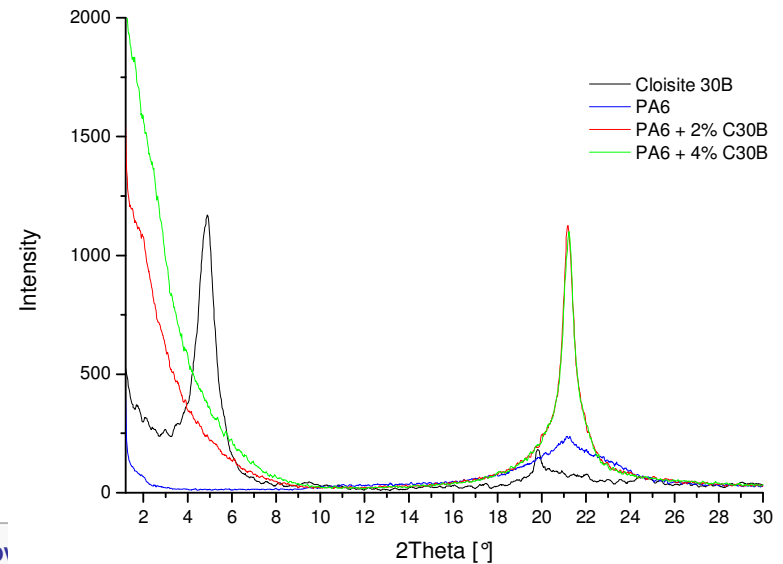
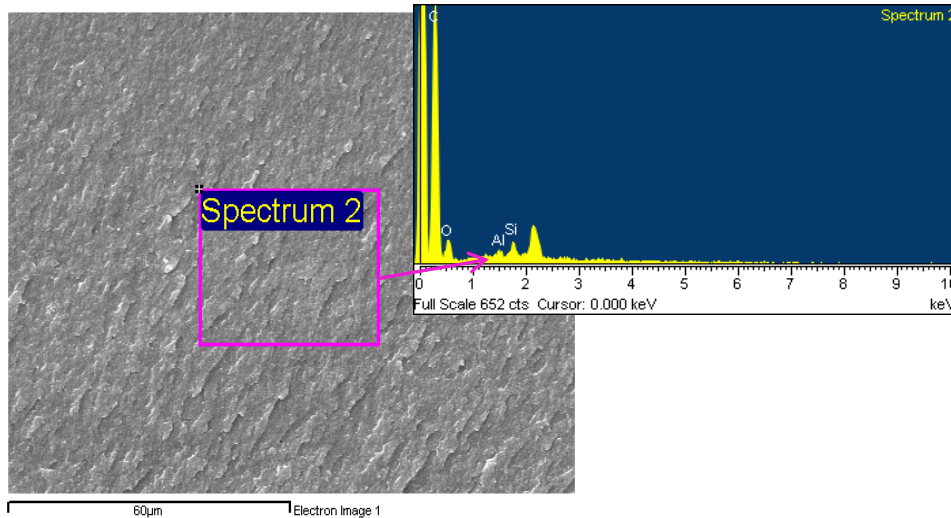
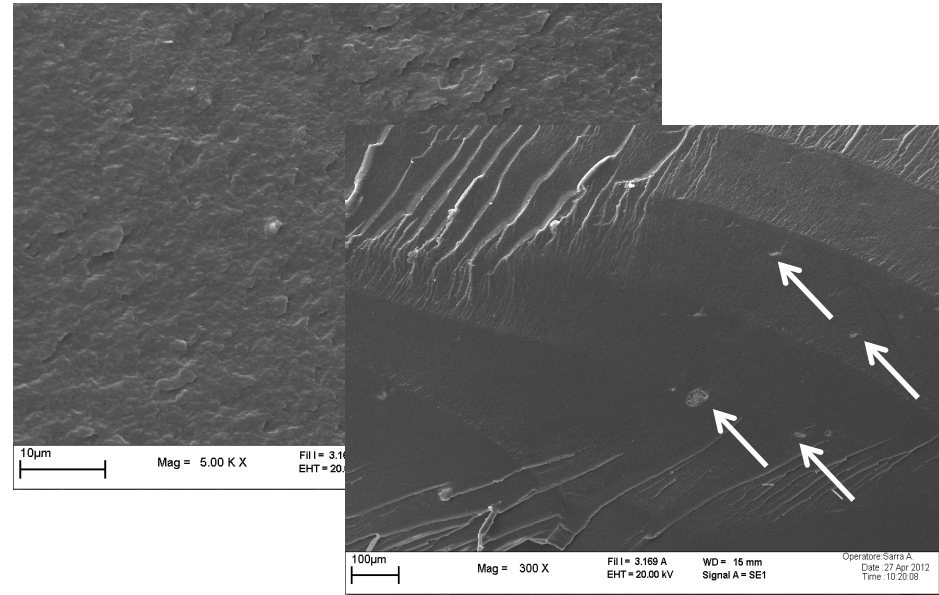


PA6 + 2% Cloisite 30B



Morphological characterization

PA6 + 4% Cloisite 30B

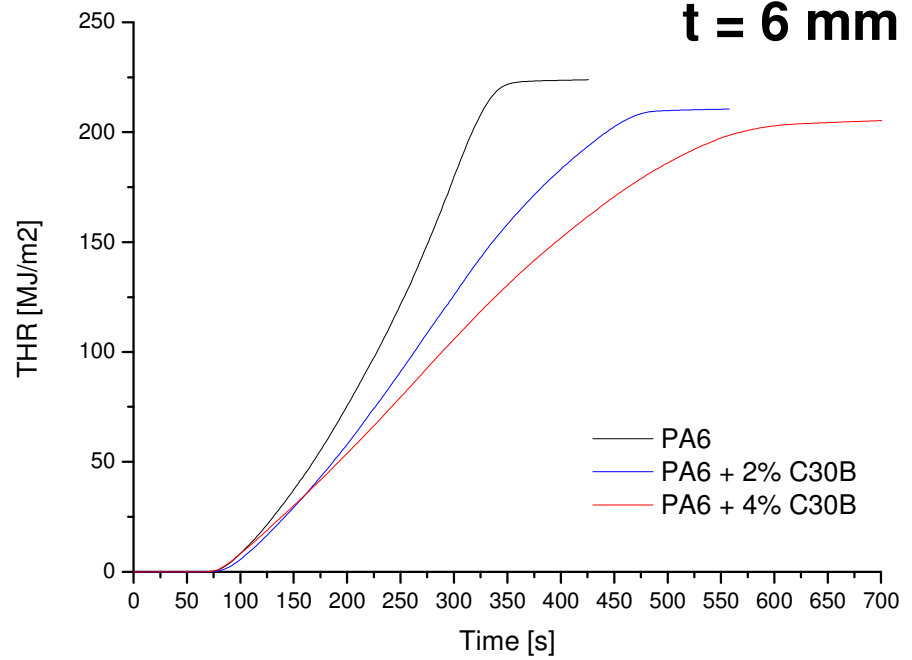
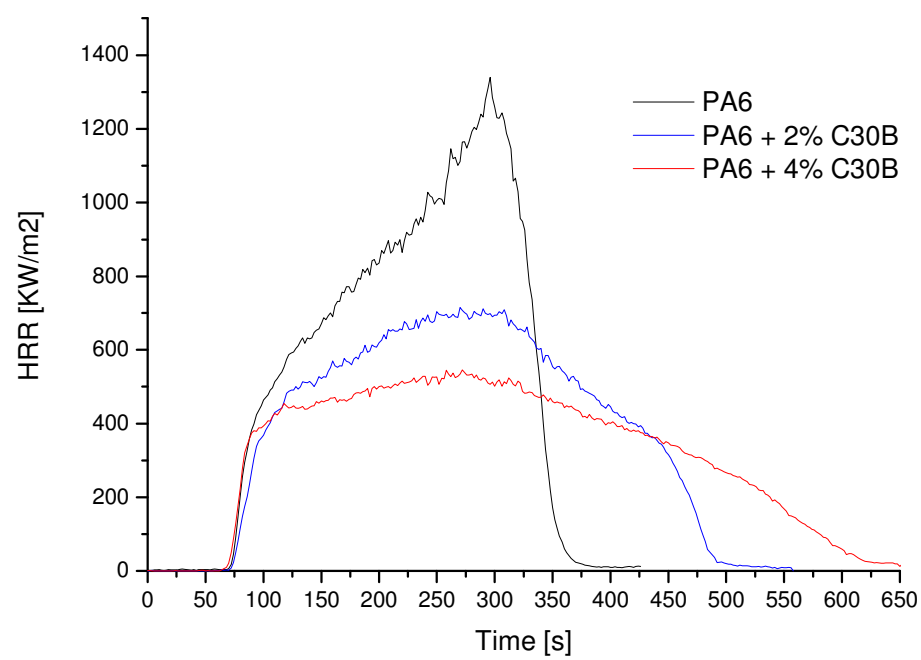






# Cone calorimeter

50 KW/m<sup>2</sup>  
t = 6 mm



MATERIAL	Time to ignition (s)	Total heat evolved (MJ/m <sup>2</sup> )	Peak of Heat release rate (kW/m <sup>2</sup> )	Total smoke released (m <sup>2</sup> /m <sup>2</sup> )	Effective heat of combustion (MJ/kg)	Avg. Carbon monoxide yield (kg/kg)	Avg. Carbon dioxide yield (kg/kg)	Residual weight (%)	Performance Index (pkHRR/TTI)
	TTI	THR	pkHRR	TSR	EHC	CO yield	CO <sub>2</sub> yield	m <sub>fin</sub> /m <sub>0</sub>	PI
PA6	75 (2)	222.3 (1.1)	1308.5 (40.3)	989.5 (44.9)	34.14 (0.16)	0.0127 (0.0010)	2.62 (0.01)	0.30 (0.07)	17.5 (0.5)
PA6 + 2% C30B	70 (4)	210.8 (1.0)	740.3 (31.1)	1461.5 (31.7)	32.46 (0.16)	0.0142 (0.0005)	2.54 (0.01)	1.80 (0.01)	10.6 (0.8)
PA6 + 4% C30B	67 (3)	203.3 (1.0)	529.8 (21.9)	1694.5 (40.5)	31.73 (0.20)	0.0149 (0.0004)	2.51 (0.01)	3.28 (0.09)	7.9 (0.2)

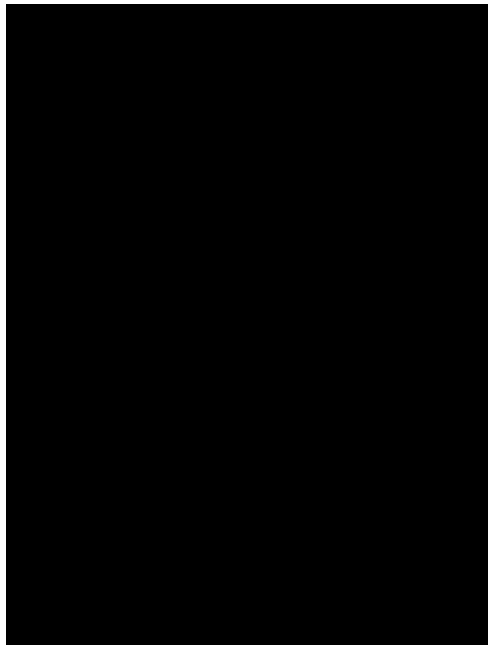


# Vertical burning test - UL94

Detachment of flaming fragments

Material	Total burning time (t1+t2) (s)	Residual mass (%)	Afterflame up to the holding clamp	Cotton indicator ignited by flaming particles or drops	UL-94 Classification
PA6	256 ± 177	38 ± 41	2/5 samples	5/5 samples	NC
PA6 + 2% C30B	35 ± 13	87 ± 5	0/5 samples	5/5 samples	NC
PA6 + 4% C30B	243 ± 111	-	5/5 samples	5/5 samples	NC

Neat



2%



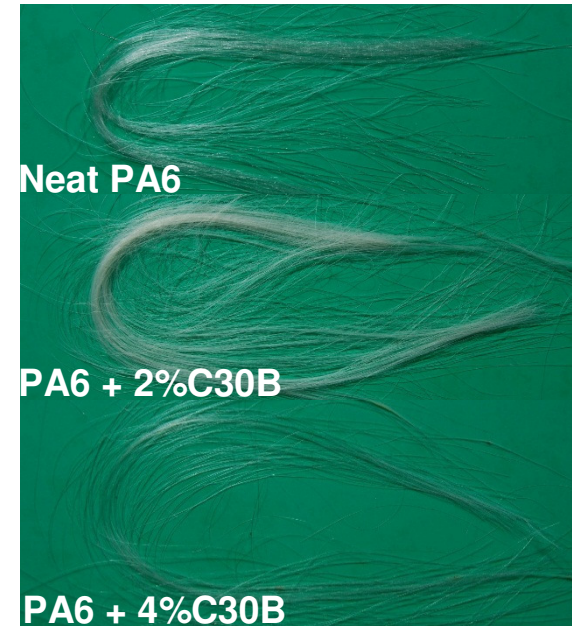
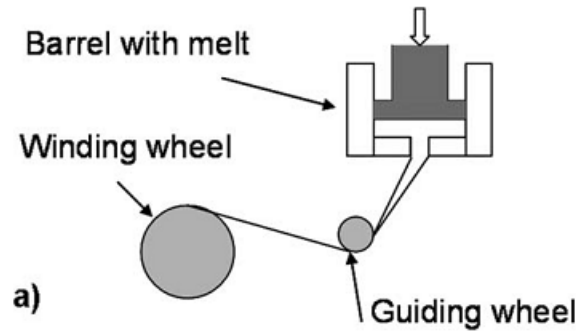
4%



# **Evaluation of drawability**

# melt draw ratio (MDR) testing

Done with a capillary rheometer **and** a spinning cylinder to wind the fibres onto



## Melt Spinning of Conducting Polymeric Composites Containing Carbonaceous Fillers

Martin Strååt,<sup>1,2</sup> Staffan Toll,<sup>1</sup> Antal Boldizar,<sup>2</sup> Mikael Rigdahl,<sup>2</sup> Bengt Hagström<sup>1</sup>

<sup>1</sup>Swerea, Department of Textiles and Plastics, Box 104, Mölndal SE-431 22, Sweden  
<sup>2</sup>Chalmers University of Technology, Department Of Materials and Manufacturing Technology, Göteborg SE-412 96, Sweden

### Summary

Material	Temperature °C	DR	Predicted Dia. Micron	Comments
PA6	230	413	98	
PA6	230	620	80	
PA6	230	258	124 (unstable)	
PA6	230	310	114 (unstable)	
PA6	230	516	88	
PA6	230	310	114	
PA6 + 2wt	230	207	139	
PA6 + 2wt	230	413	98	
PA6 + 2wt	230	723	74	Max speed for setup
PA6 + 2wt	230	723	74	Max speed for setup
PA6 + 4wt	230	83	220	Break often, difficult to get continuous fibres
PA6 + 4wt	250	516	88	Much improved over the lower temperature

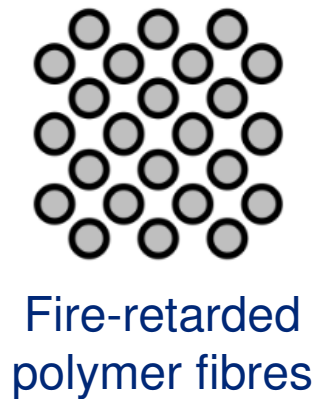
**Conclusions:**  
 Both the nanocomposite passed the drawability test and are suitable for spinning  
 2%C30B spinning is as straightforward as the neat polymer – 4%C30B is more complicated

→ **SELECTED MATERIAL: PA6+2%C30B**

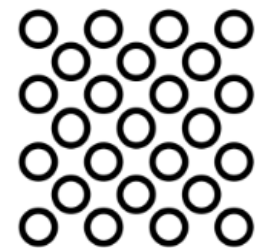
# **Fiber reinforced PA6 production**

# Production steps

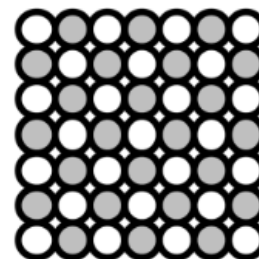
1. Polymeric fiber **spinning**
2. **Commingling**
3. **Consolidation**



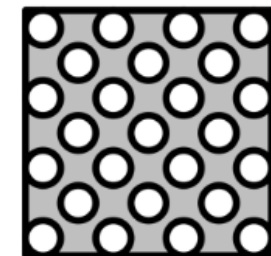
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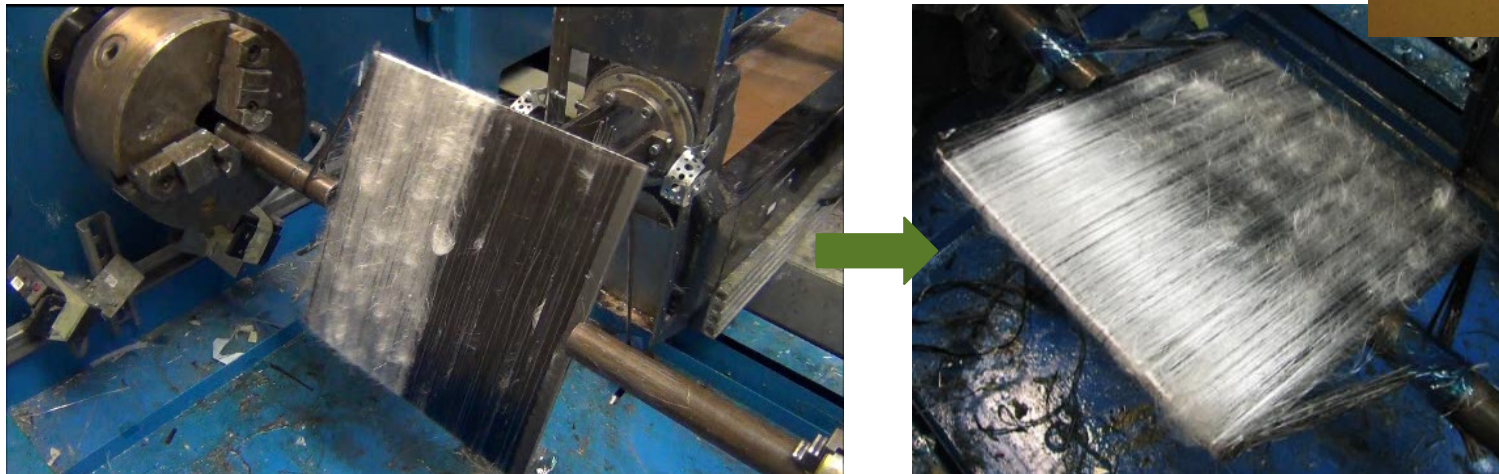
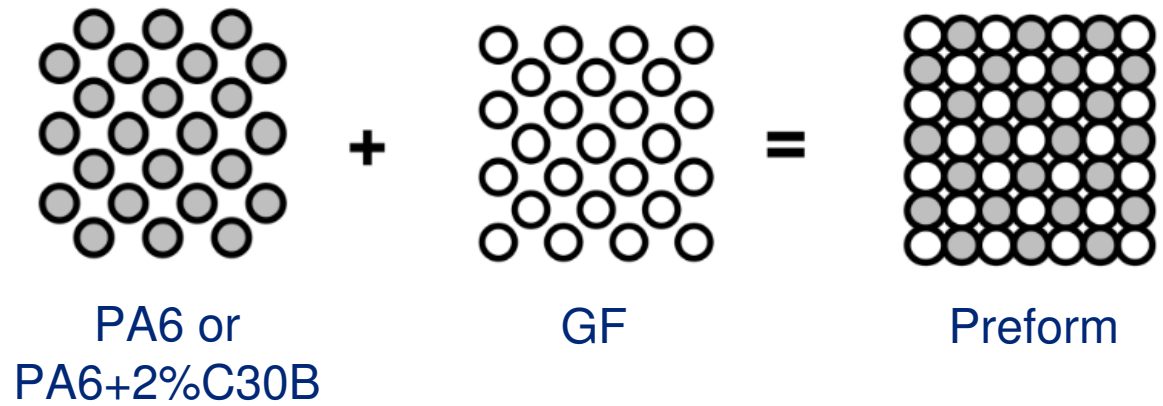
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Consolidation

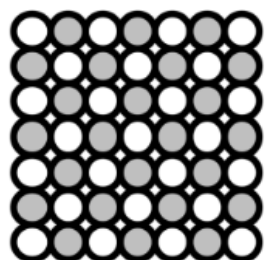


# Commingling procedure

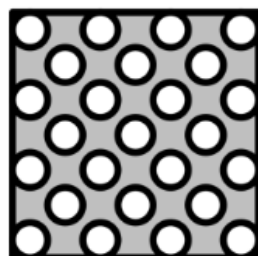




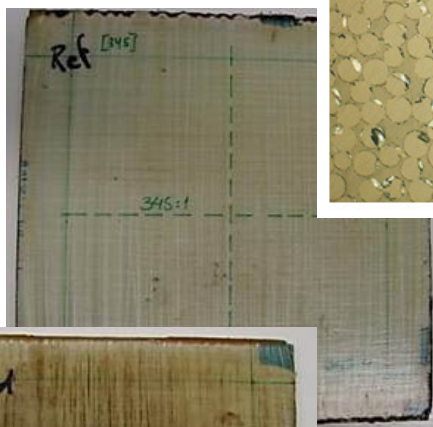
# Consolidation



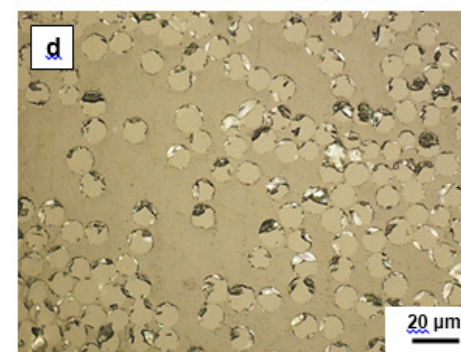
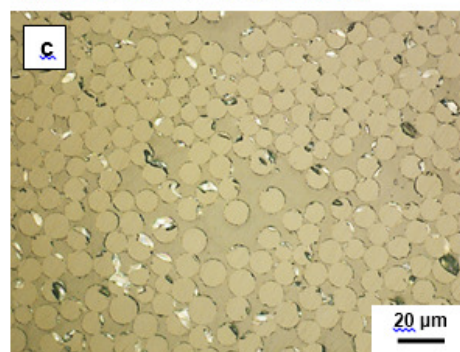
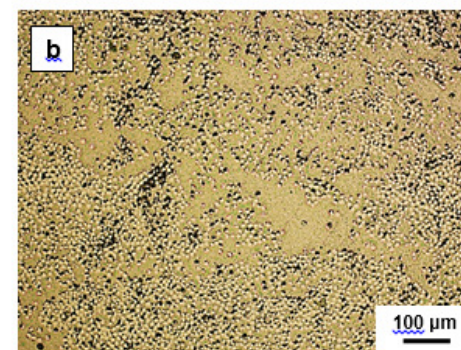
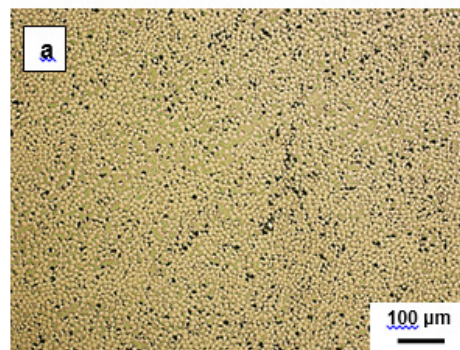
G/PA6 (doped or not) preform



Composite laminate



230x230x2-3 mm

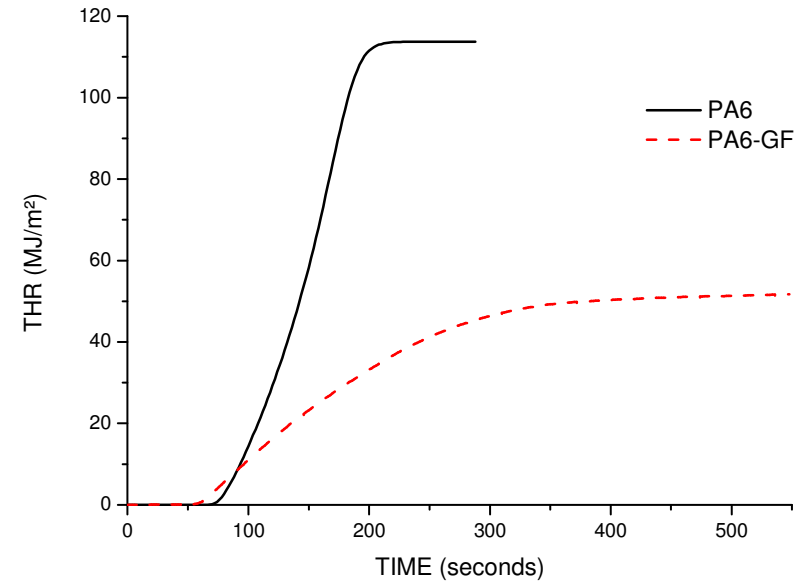
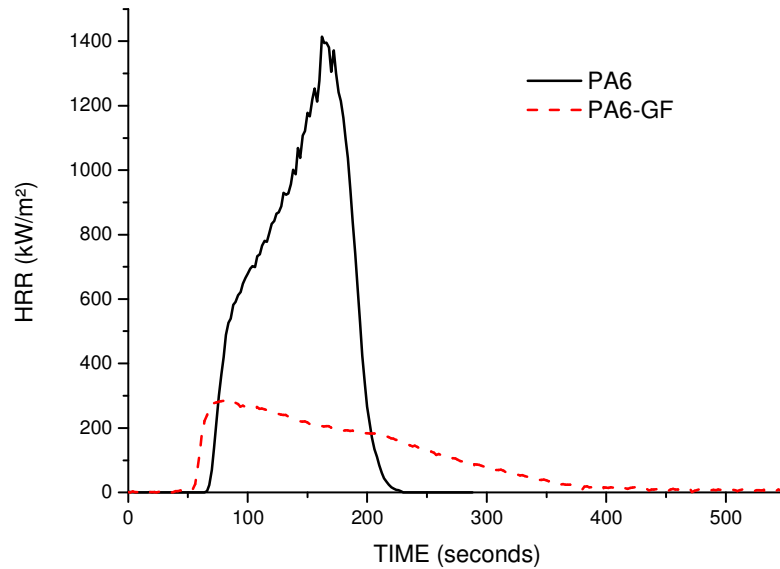


Material	mass residue (%)	G/volume fraction (%)
G/PA6	73.1%	55.1%
G/PA6+2%C30B	70.6%	51.9%



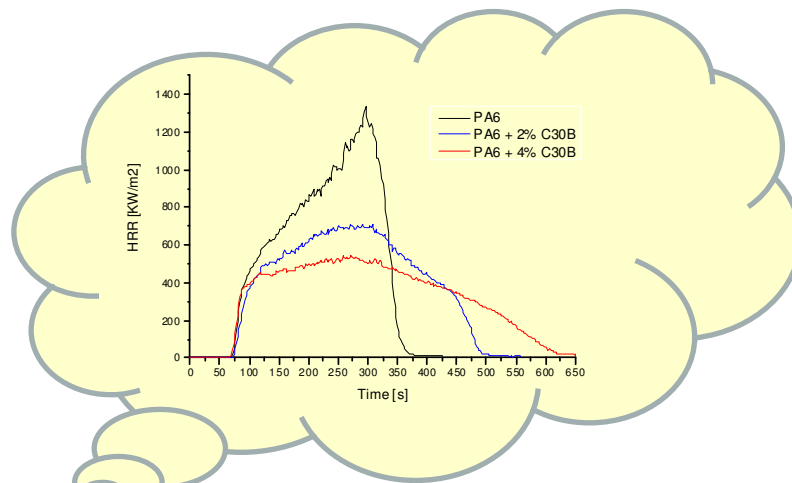
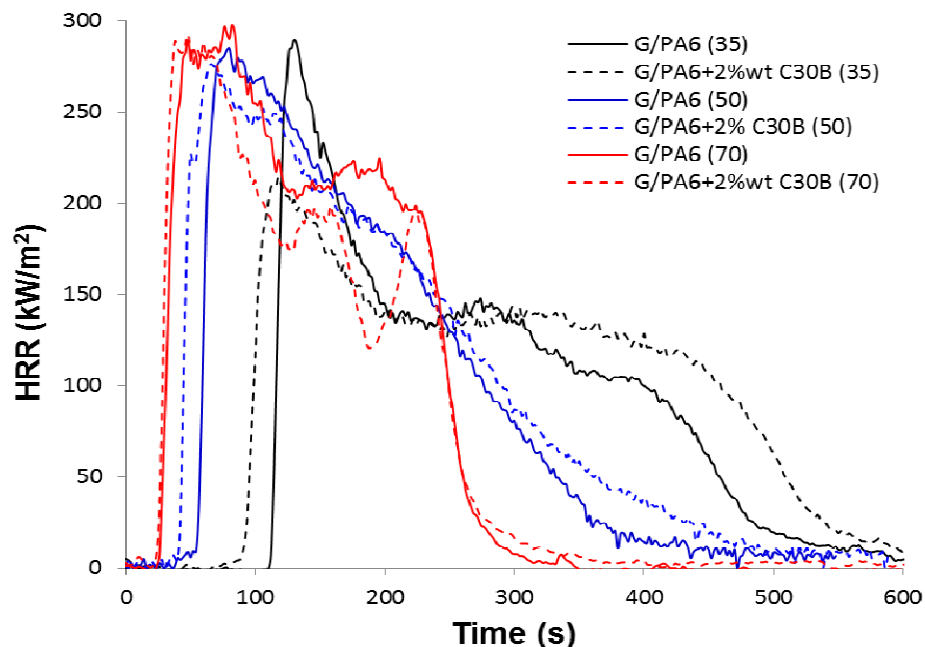
# Characterization

# Effect of GF on the fire behavior of PA6



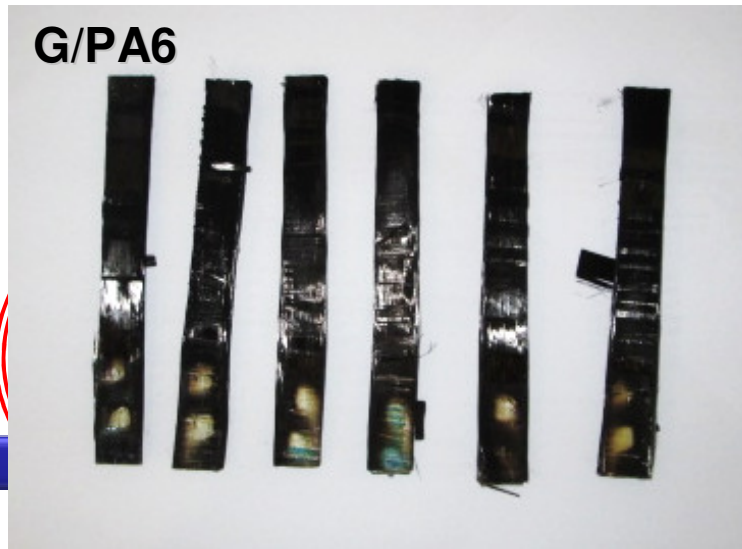
1. Reduction of the HRR peak and THR
2. Change from non-charring behaviour to charring behaviour
3. Earlier combustion (lower TTI)

# Cone calorimeter

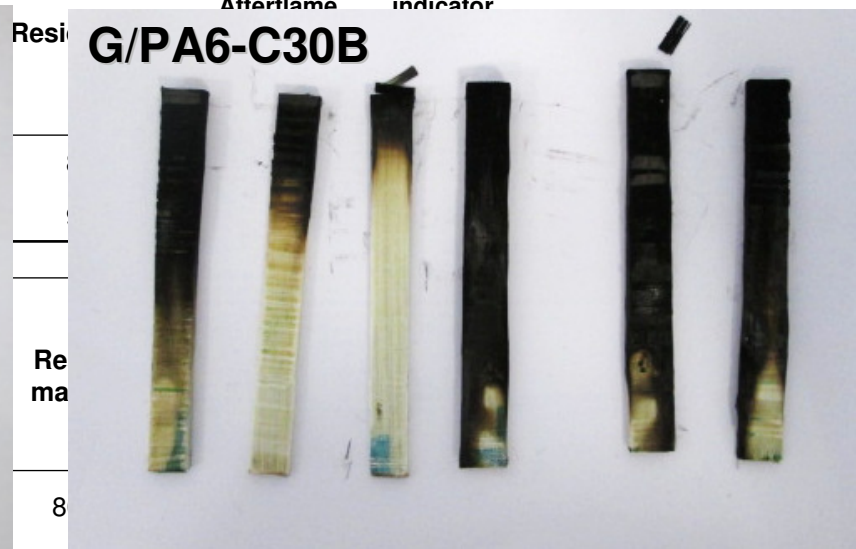


MATERIAL	Time to ignition (s)	Total heat evolved (MJ/m <sup>2</sup> )	Peak of Heat release rate (kW/m <sup>2</sup> )	Total smoke release (m <sup>2</sup> /m <sup>2</sup> )	Effective heat of combustion (MJ/kg)	Avg. Carbon monoxide yield (kg/kg)	Avg. Carbon dioxide yield (kg/kg)	Residual weight (%)	Performance Index (pkHRR/TTI)	Maximum Average Rate of Heat Emission (KW/m <sup>2</sup> )	Fire growth rate (pkHRR/time@pkHRR)
	TTI	THR	pkHRR	TSR	EHC	CO yield	CO2 yield	m <sub>fin</sub> /m <sub>0</sub>	PI	MAHRE	FIGRA
G/PA6 (50)	59 (4)	53.1 (4.1)	296.1 (11.2)	268.4 (59.0)	59.61 (7.15)	0.0166 (0.0021)	5.38 (0.58)	85.03 (1.36)	5.1 (0.5)	174 (13)	3.9 (0.3)
G/PA6+2%C30B (50)	50 (1)	58.2 (1.5)	272.6 (17.8)	307.3 (13.3)	71.76 (11.76)	0.0245 (0.0027)	6.45 (1.08)	86.45 (2.27)	5.4 (0.3)	174 (8)	4.2 (0.2)

# Vertical burning test - UL94



**G/PA6**



**G/PA6-C30B**

Afterflame Cotton indicator

Resi

Re  
ma

8

**G/PA6+2%C30B**

28 ± 24

89 ± 21

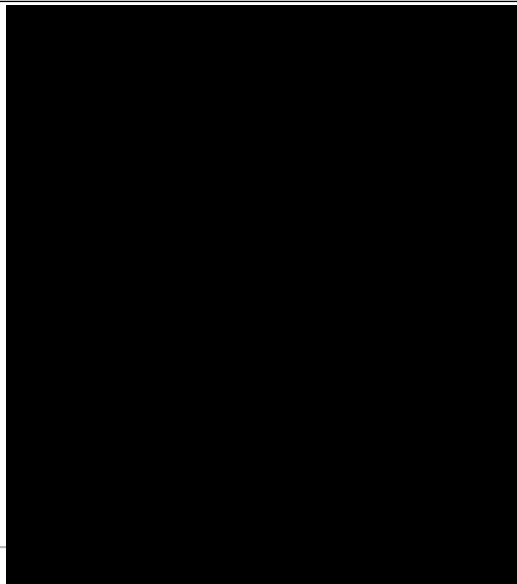
97 ± 2

0/3 samples

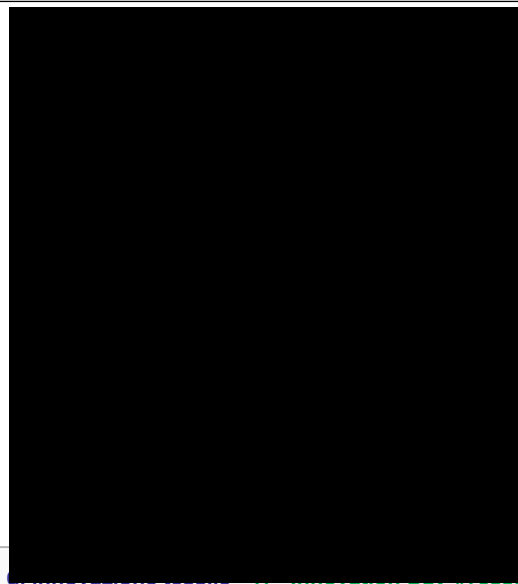
0/3 samples

NC

**G/PA6**



**G/PA6-2%C30B**





## Goal

To understand the role of nanoclay in the combustion behavior of PA6, since the effect is different with or without GF, by verifying the hypothesis that NCs migrate to the exposed surface before ignition

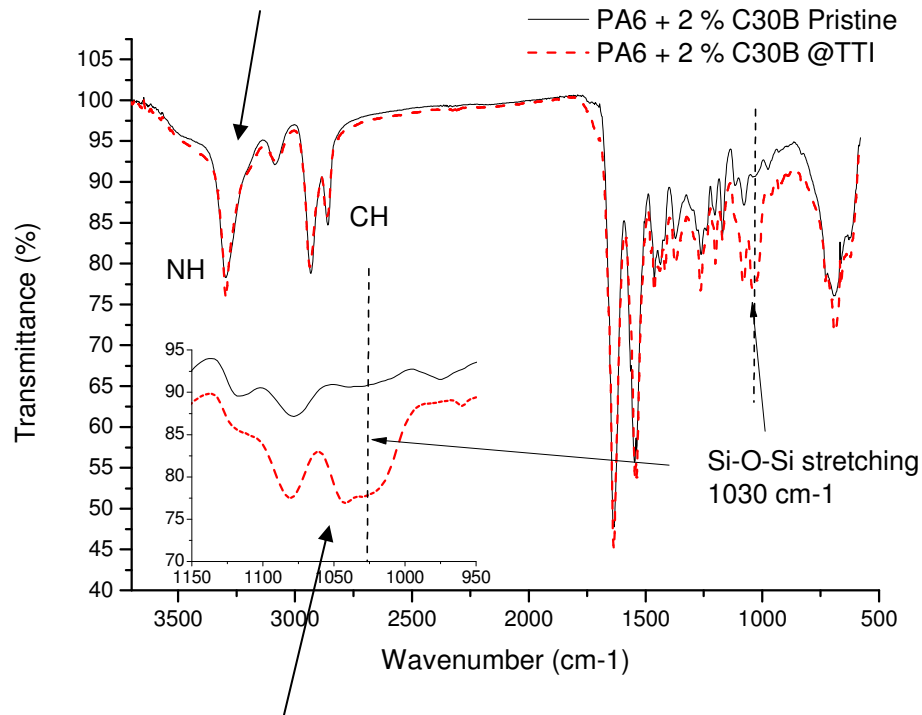
## Test condition

Cone calorimeter tests were carried out (50 KW/m<sup>2</sup>) up to ignition and then flaming was stopped through N<sub>2</sub> flux

## Sample characterizations

Mid-Infrared (ATR)

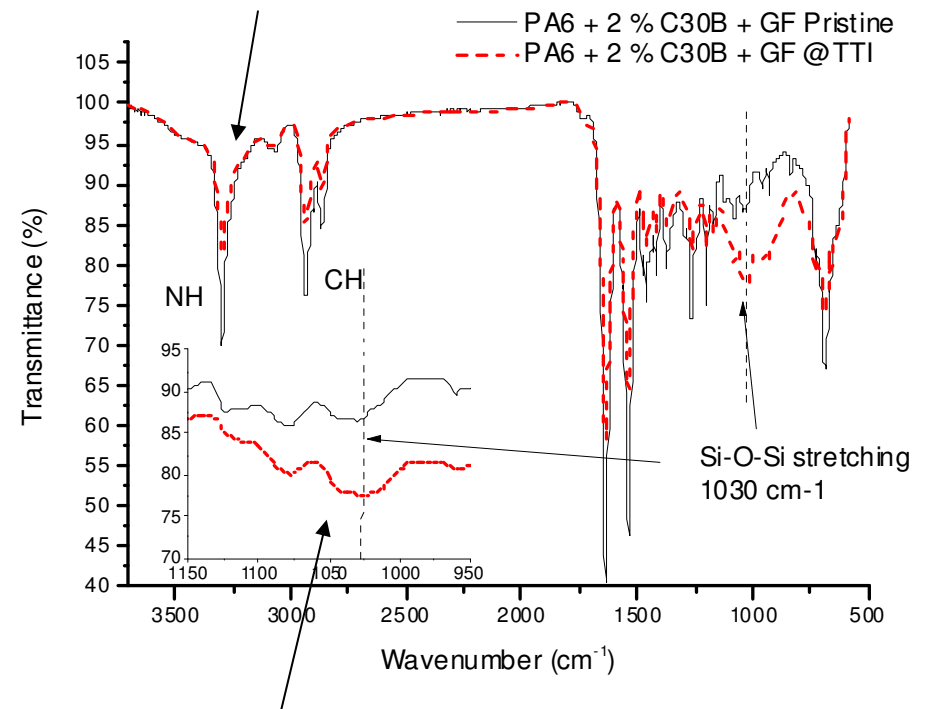
## No differences in the matrix



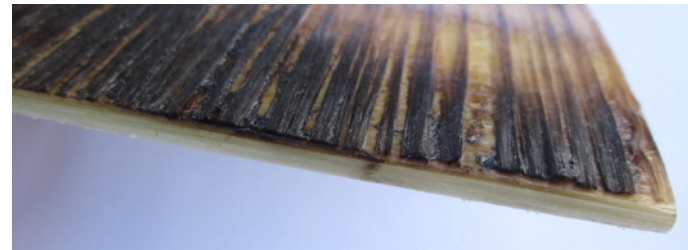
Increase in the Si-O-Si peak area



## Reduction of the matrix



No difference in the Si-O-Si peak





- Il commingling si rivela essere una **buona tecnica di produzione** di composite termoplastici in fibra continua. In particolare, è efficace per aggiungere cariche – di natura nanometrica – al composito finale per via della semplificazione del processo.
- Sebbene **la nanoargilla riesca a migliorare notevolmente le proprietà al fuoco della PA6**, in combinazione con le fibre di vetro questo effetto è meno netto e comunque di **natura diversa**.
- La **corretta progettazione** di un sistema composito multiscala può condurre a miglioramento delle prestazioni od anche all'aggiunta di caratteristiche non presenti inizialmente. Tuttavia tale progettazione va affrontata in modo consapevole partendo dal presupposto che le interazioni polimero/fibra/nanocarica vadano studiate contemporaneamente piuttosto separatamente.





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# Grazie dell'attenzione!

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