Cables 2007

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What is new for flame retardancy by nanotechnology ?

What is new in flame retardancy by nanofillers ?

Cable applications with FR *by nanofillers*

Topics of the presentation

- Flame retardancy by nanocomposites
- New flame retardants based on nanostructured fillers
- Pro/Contra examples of nanotechnology based cables
- Summary

Transfer to « Reality »

- Organoclays alone are **not** sufficient flame retardants
- There is a strong **synergistic effect** between the classical flame retardants and **<u>organoclays</u>**
- **Halogen or non-halogen** flame retardants can be used
- **Organoclay** are **<u>char promotors</u>**
- Nanocomposites-based compounds by **filler combinations** with ATH or MDH are already used for typical cable **EVA / LDPE polmyerblends** since few years

Prof. Charles Wilkie

Department of Chemistry,
Marquette University,
Milwaukee, WI, USA

If you have an impressive reduction of heat release by

only few percentages of a filler, then the filler is nanodispersed !!

The organoclay within the polymer matrix can change the degradation pathway !!

- **PS, EVA or PA**

large reduction in PHRR, observation of different decomposition products or different quantities of decomposition products; stable radicals by degradation & then recombination (char formation)

- **PMMA**

smaller reduction in PHRR, single degradation pathway, no promotion of different pathways, only barrier effect of the organoclay

Prof. Menachem Lewin

Polytechnic University
Brooklyn, NY, USA

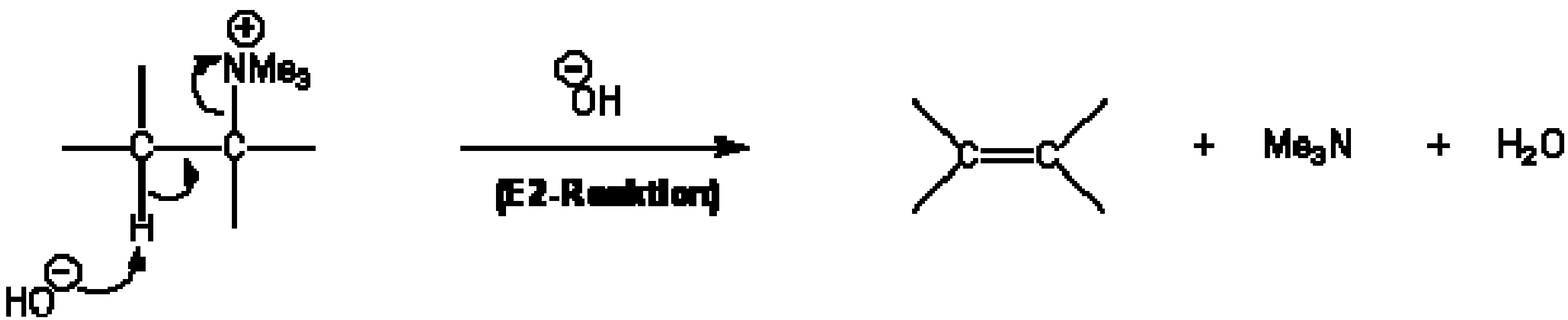
Decomposition of the surfactant in the clay above 200^{o}C with 2 simultaneous and opposing phenomena:

- *migration of the clay to the surface*
- *conversion of the nanocomposite into a microcomposite*

=> *barrier formation & reduction of PHRR*

Extrusion problems @ > 200°C

Hofmann - degradation of tetra-alkylammonium ions



- Formation of an alkene (=> low mol. weight & burnable !!)

Possibles alternative nanofiller by layered double hydroxides

Layered double hydroxides (LDHs) have the general formula :

$$M^{2+}_{(1-x)}M^{3+}_{x}(OH)]A^{n-}_{(x/n)}\cdot mH_2O$$

M^{2+} and M^{3+} can be any metal cation with an ionic radius equal to or less than that of Ca^{2+}.

The charge balancing anion, A^{n-}, can be nearly any inorganic or organic anion

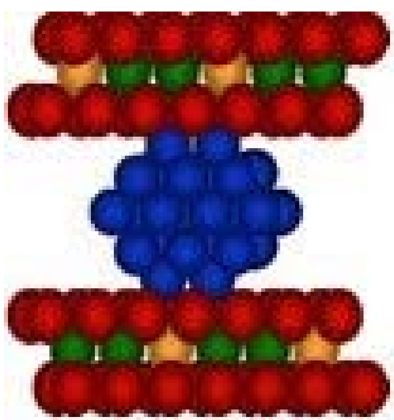


Figure1. Schematic of an LDH.

much more thermal stable modifiers than the quat.ammonium compouds

LDH in flame retardancy

Nano-dispersed LDH allows to combine the flame retardant effect of both inorganic hydroxides and layered crystal nanocomposites

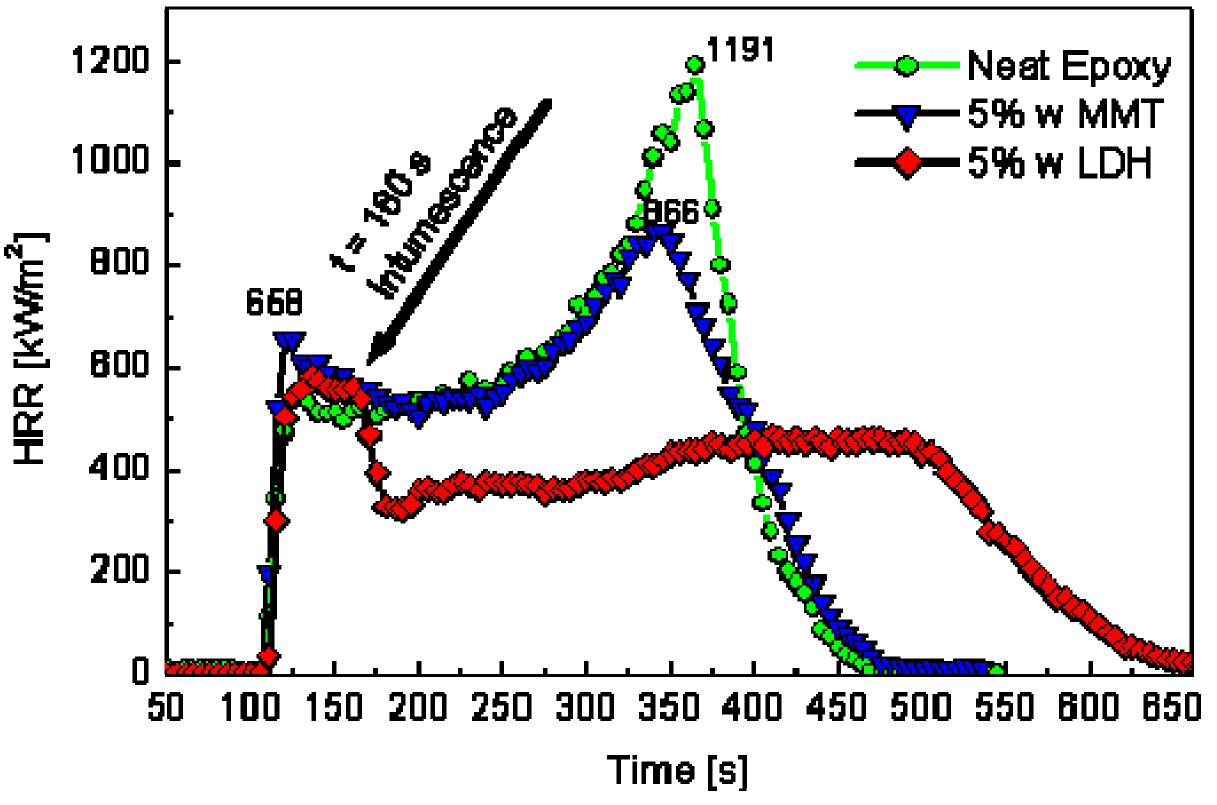
Inorganic Hydroxides

- Endothermic decomposition
- Some ceramic residue
- Dilution of the combustible gases
- Decrease of CO/CO_2 ratio

Layered Crystal Nanocomposites

- Barrier effect
- Reduced HRR

Cone Calorimetry



LDH nanocomposites show an **intumescent behavior**

52 % (!!) reduction in the PHRR for LDH nanocomposite

Only 20 % reduction in the PHRR for MMT nanocomposites

Possibles alternative nanofiller by layered double hydroxides

Cationic clays

(e.g. montmorillonite)

Surface charge density: $\sigma \approx$ **0.007** $e^- / Å^2$

Less electrostatic attractive forces between layers

easy dispersion

Anionic clays

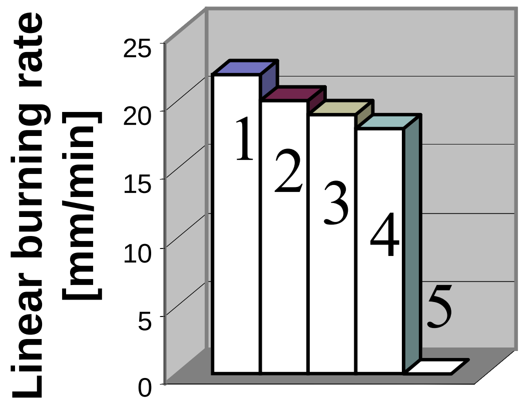
(e.g. layered double hydroxides)

Surface charge density $\sigma \approx$ **0.02 ÷0.1** $e^- / Å^2$

Severe electrostatic attractive forces between layers

more difficult dispersion

Flame Resistance

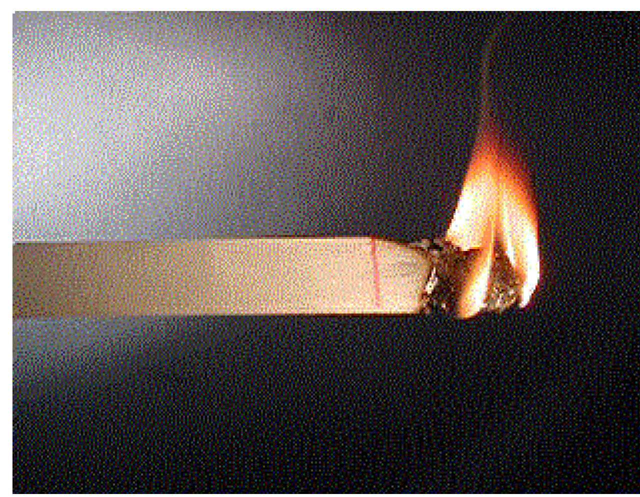


- 1: Neat Epoxy Resin
- 2: 5 wt.% MMT (Cloisite 30B)
- 3: 5 wt.% ATH (Apyral 40)
- 4: 5 wt.% LDH (Inorganic form) Microcomposite
- 5: 5 wt.% organo-LDH Nanocomposite

Micrometric dispersion LDH

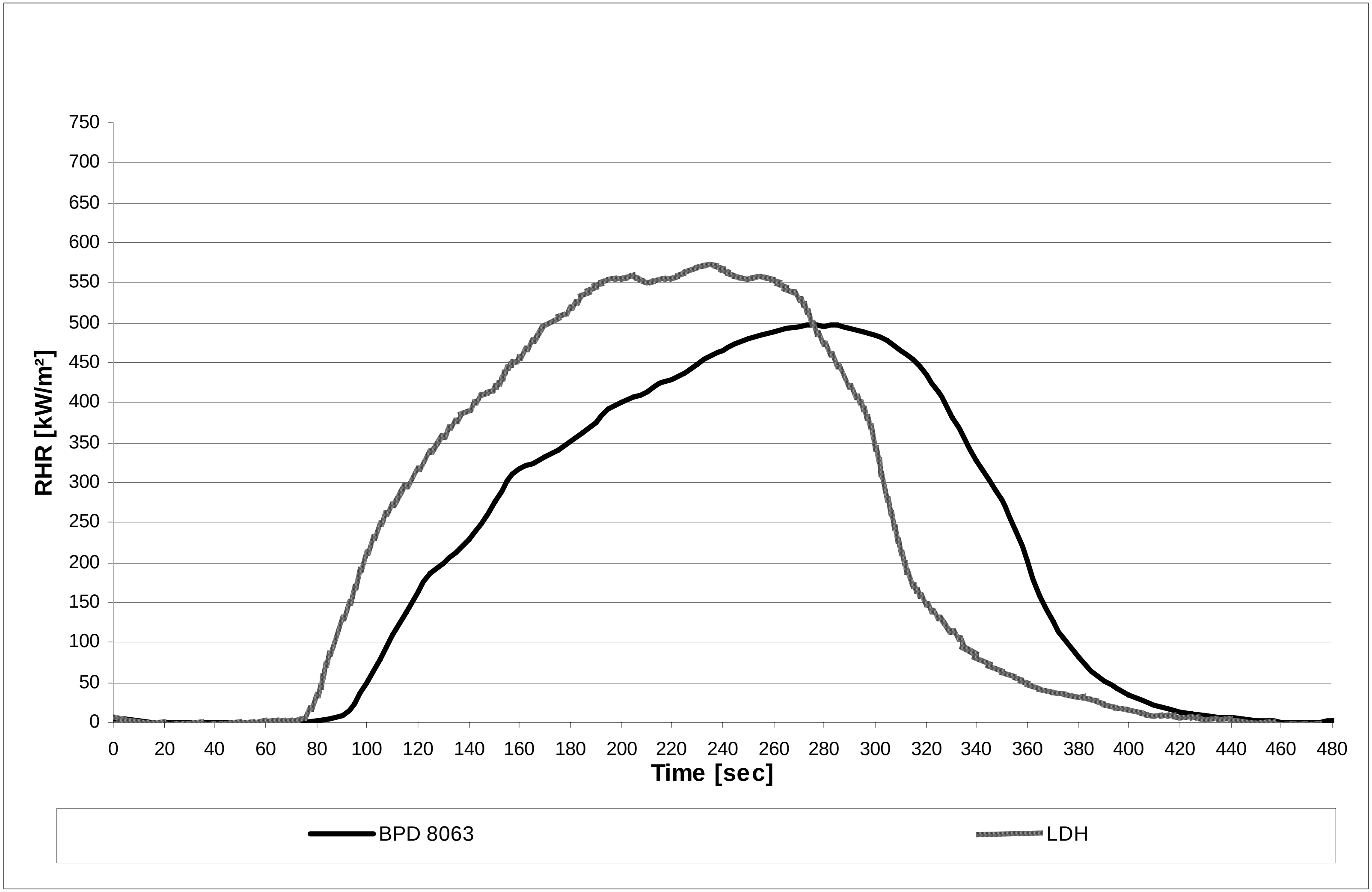
5 wt.% LDH (carbonate form); d ≈ 7.6Å

Nanometric dispersion LDH

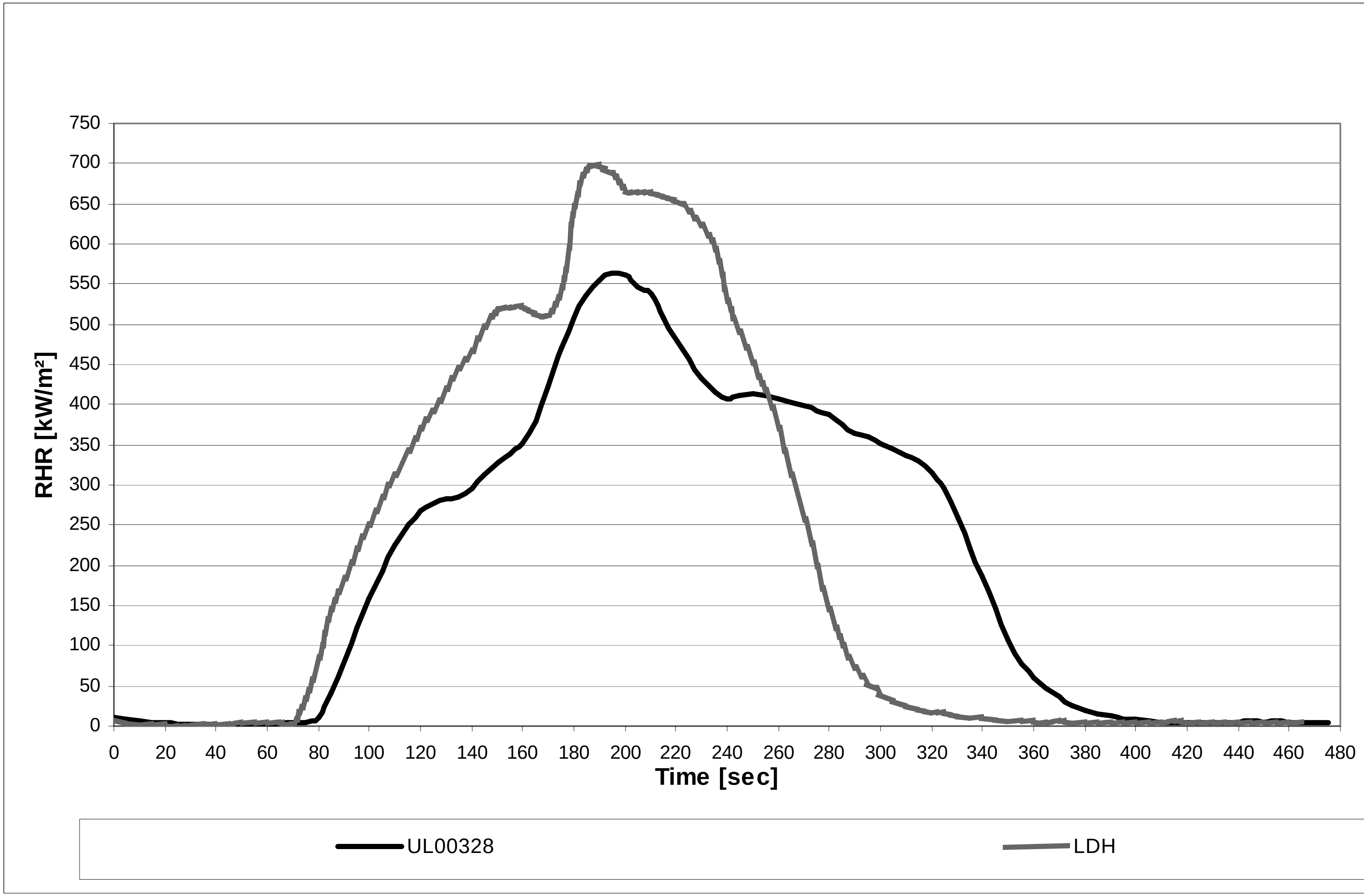


5 wt.% organo-LDH; d ≈ 28.3Å

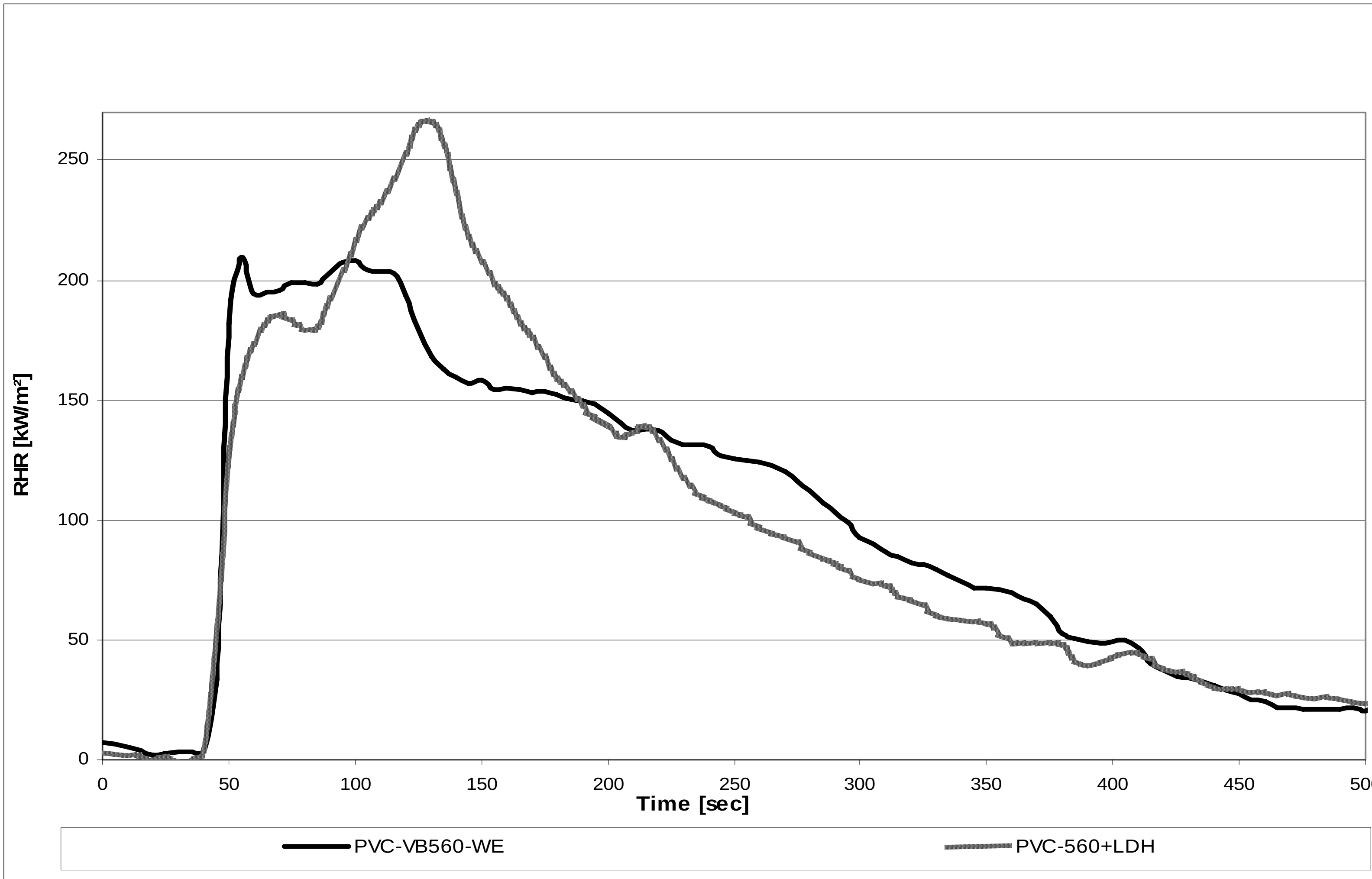
LDPE + 5 % LDH via Brabender
35 kW m^{-2}



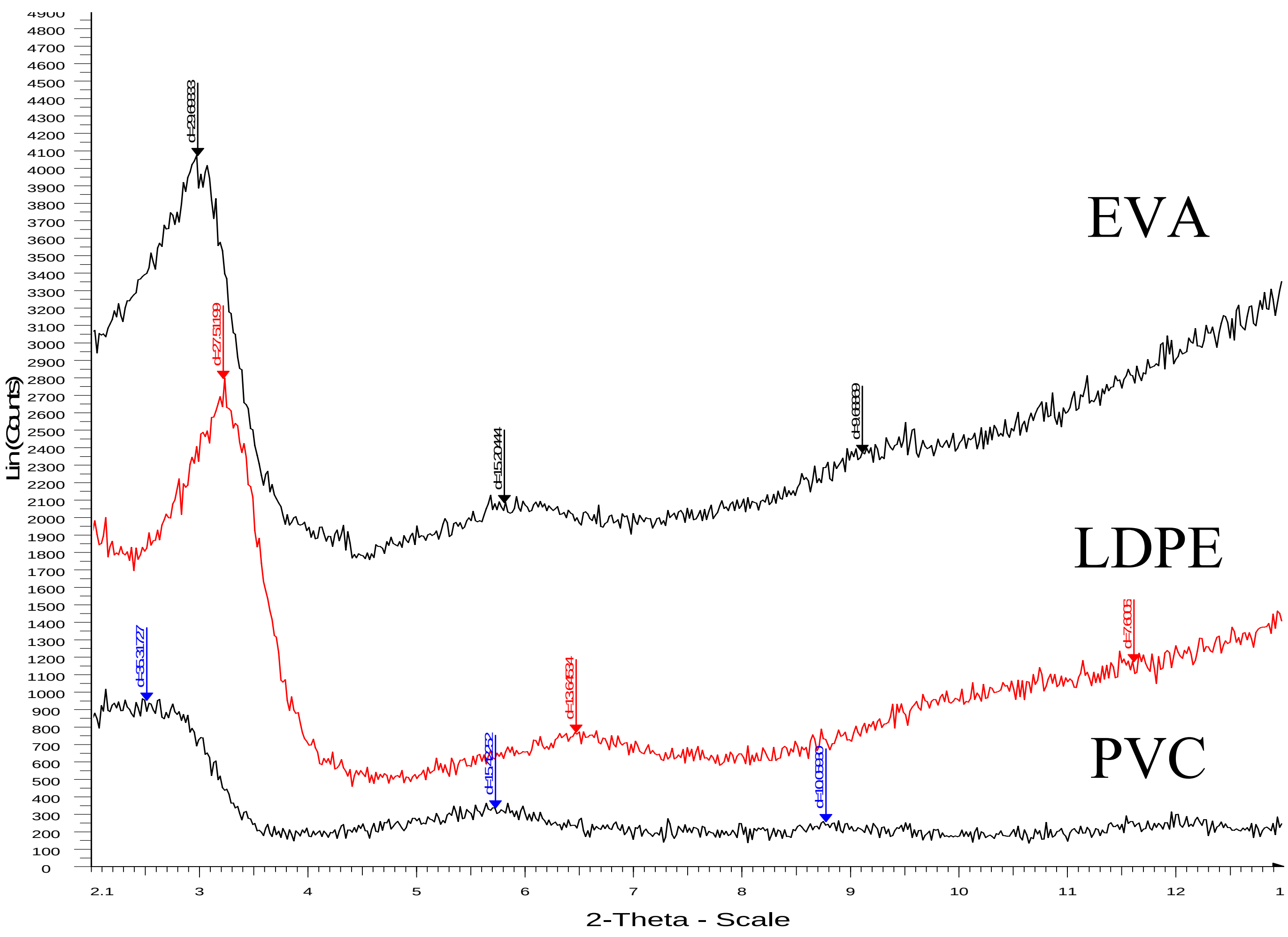
EVA + 5 % LDH via Brabender
35 kW m^{-2}



flexible PVC + 5 % LDH via Brabender
35 kW m^{-2}



XRD-investigation / Brabender compouding



Next tests with higher shear rates to overcome

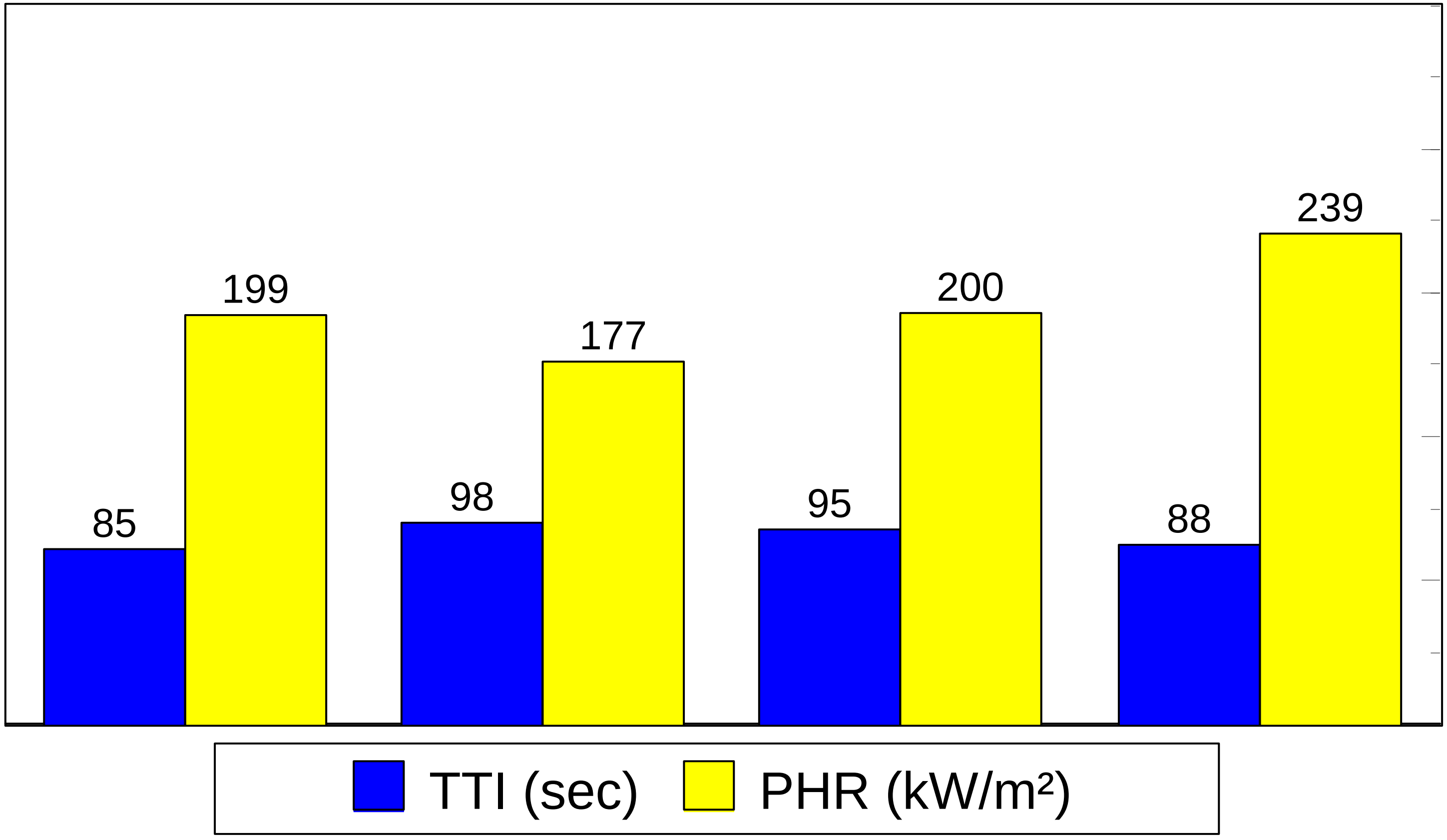
the strong electrostatic forces within the LDH

by corotating twin screw extruder

are under progress …..

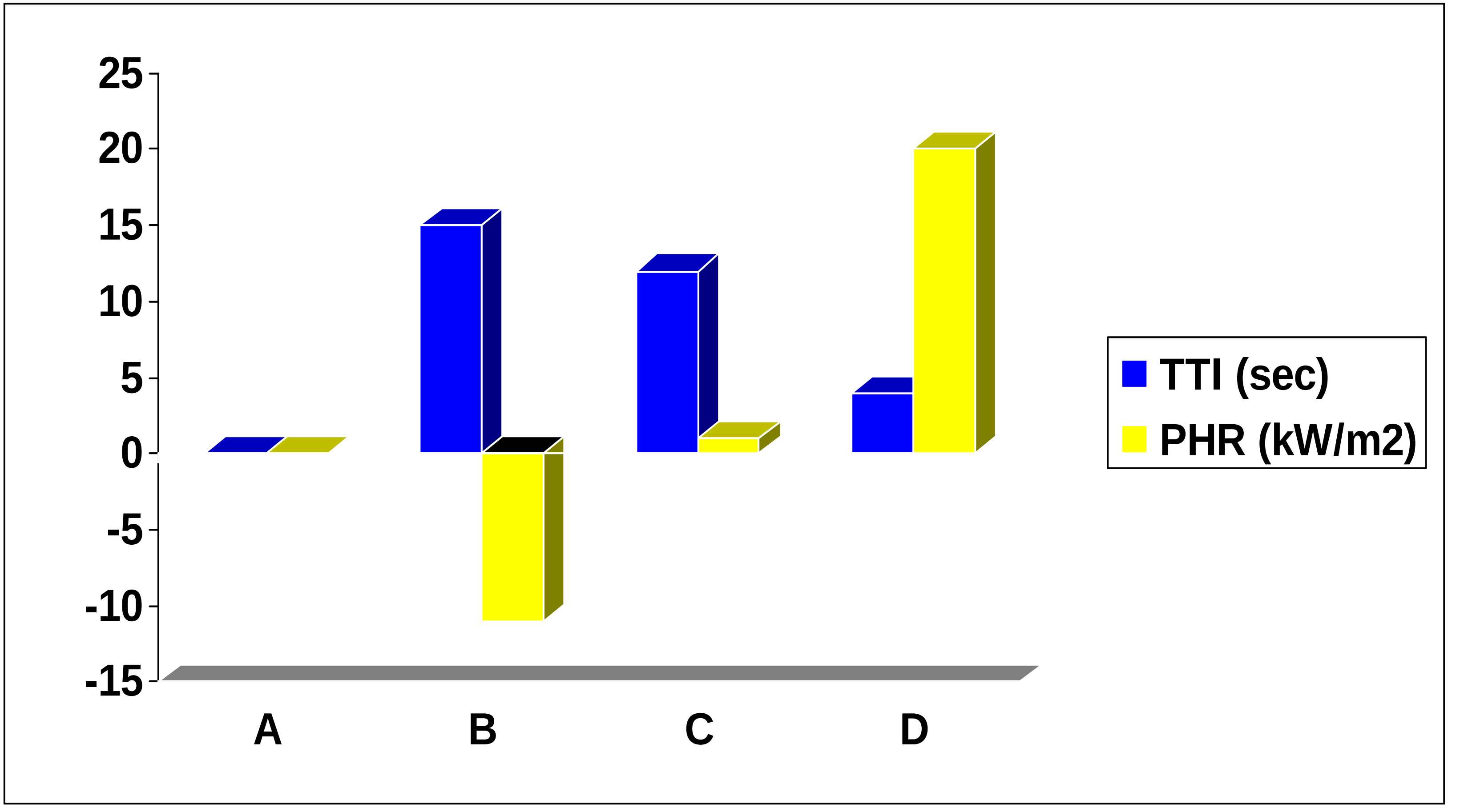
Values for TTI & PHR of ATH compound and nanocomposites

A: 100 polymer + 150 ATH (reference)
B: 100 polymer + 150 ATH + 5 organoclay
C: 100 polymer + 130 ATH + 5 organoclay
D: 100 polymer + 90 ATH + 5 organoclay



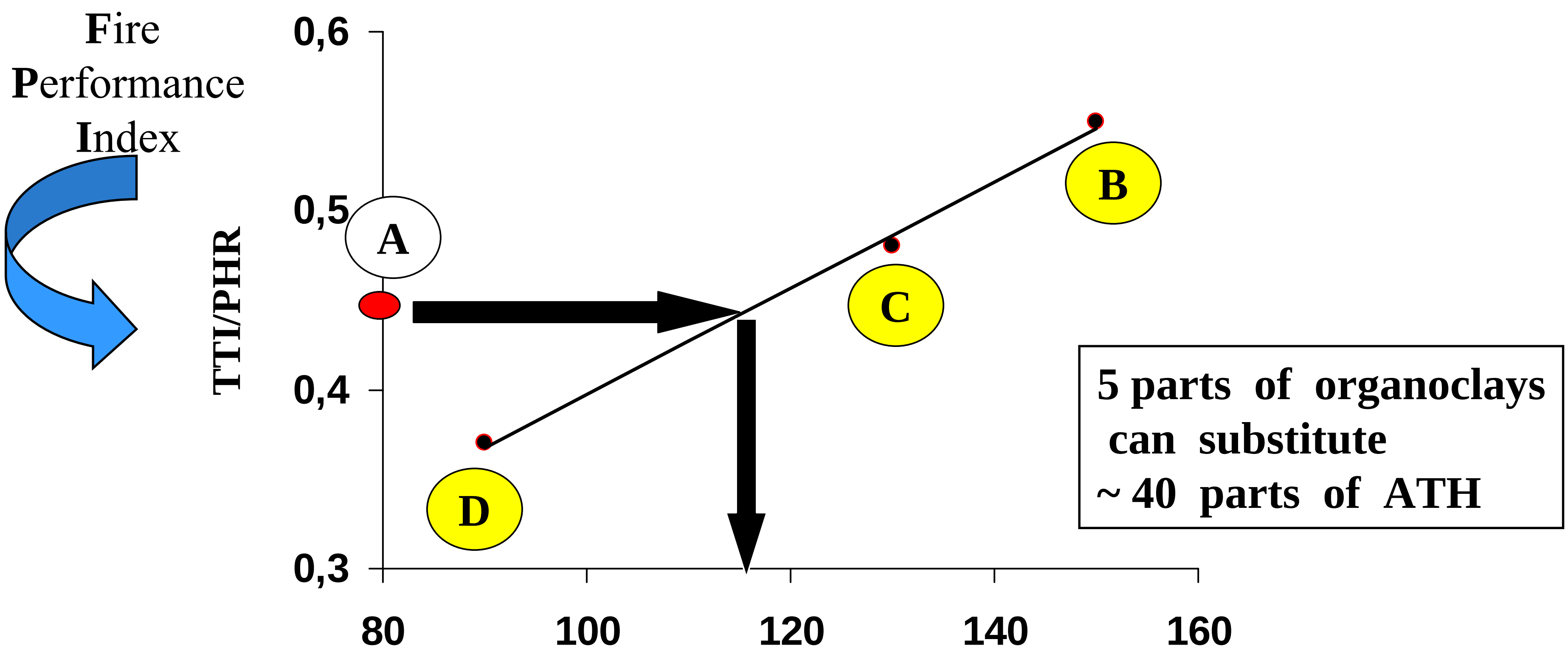
% changes of values for TTI & PHR of ATH compound
and nanocomposites related to the values of the ATH compound

A: 100 polymer + 150 ATH (reference)
B: 100 polymer + 150 ATH + 5 organoclay
C: 100 polymer + 130 ATH + 5 organoclay
D: 100 polymer + 90 ATH + 5 organoclay



FPI values of ATH compound and nanocomposites in relation to the content of the ATH

A: 100 polymer + 150 ATH (reference)
B: 100 polymer + 150 ATH + 5 organoclay
C: 100 polymer + 130 ATH + 5 organoclay
D: 100 polymer + 90 ATH + 5 organoclay



Is it possible to reduce dramatically the amount of ATH in FRNH-compounds by using organoclays ?

Result : YES

Calculation and prediction via Fire Performance Index :

ca. **40** parts ATH in a FRNH cable jacket can be substituted by **5** parts of a suitable organoclay without reduction in fire performance properties

We have checked this prediction by producing 2 identical cables with 2 different jackets:

- Jacket A : (100 polymer + 150 ATH)

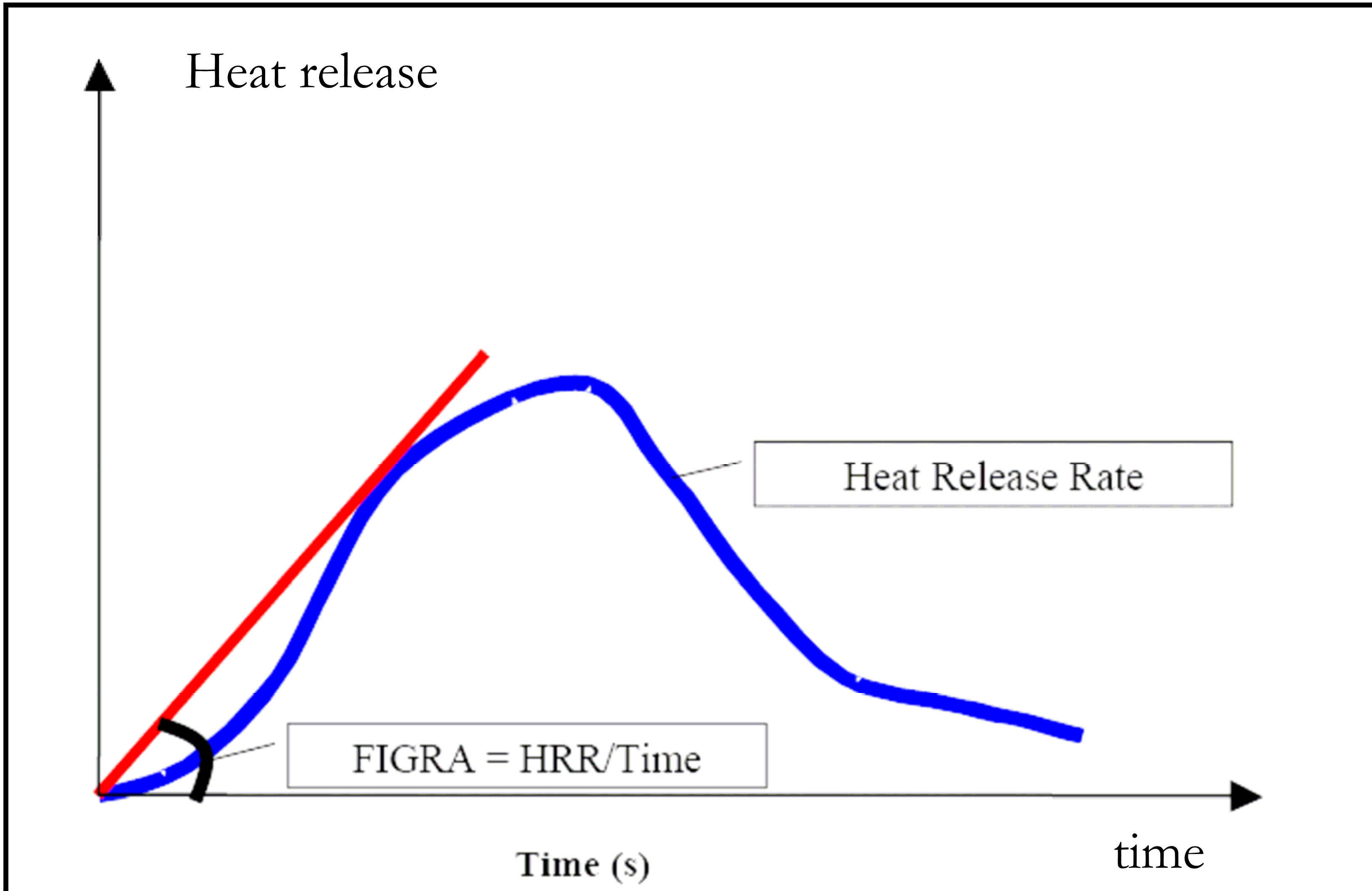
- Jacket B : (100 polymer + 110 ATH + 5 organoclay)

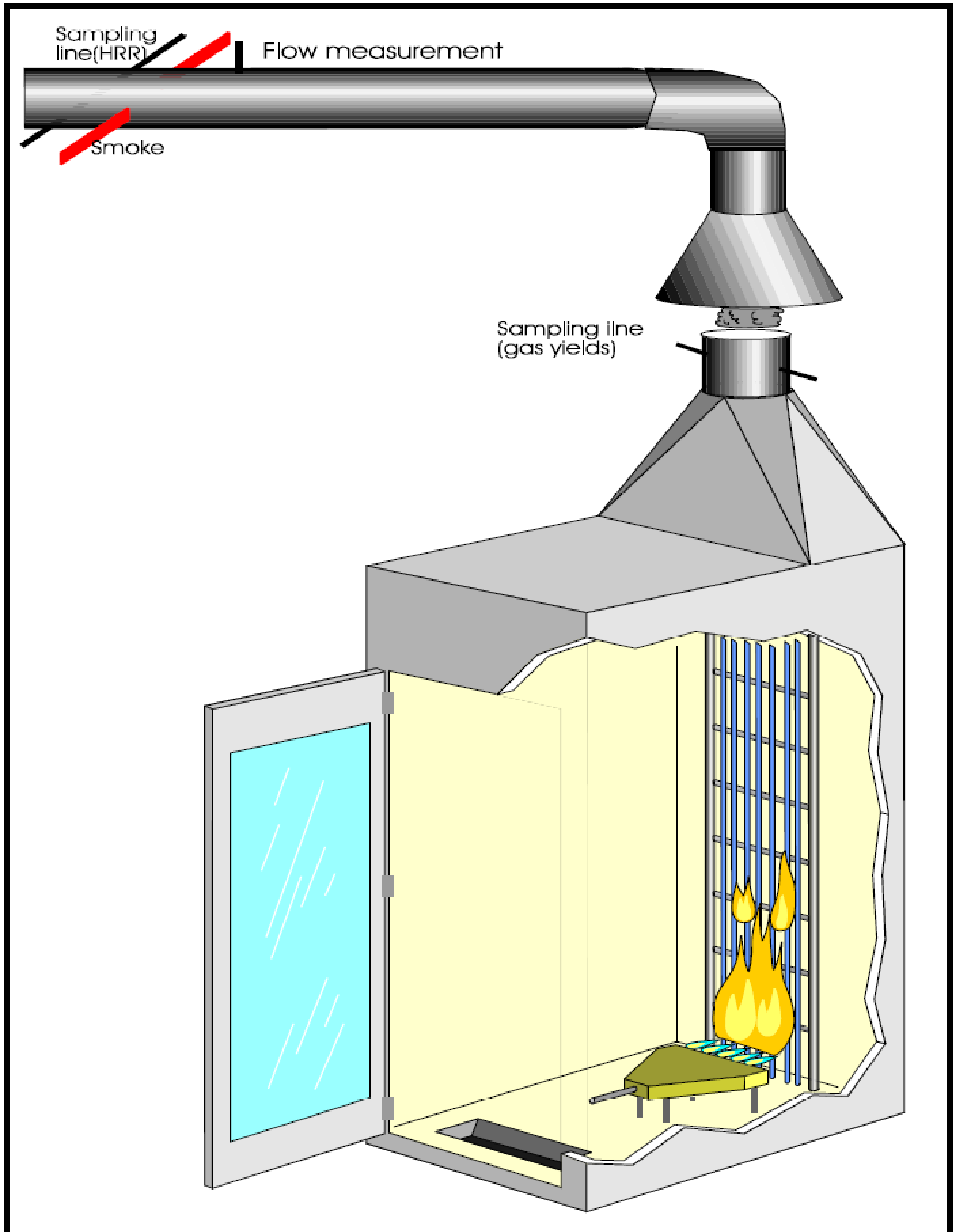
Jacket	Smoke density	Flame propagation	
	IEC 61034	small scale IEC 60332-1	large scale IEC 60332-3 C
Jacket A	85 %	12 cm Char: +/-	70 cm Char: +/-
- 40 phr ATH + 5 phr organoclay			
Jacket B	85%	11 cm Char: +	100 cm Char: +

Table "Euroclasses cables" by FIPEC

Class	Test method(s)	Classification criteria	Additional classification
A_{ca}	EN ISO 1716	PCS ≤ 2,0 MJ/kg (1) *and* PCS ≤ 2,0 MJ/kg (2) *and*	
$B1_{ca}$	$FIPEC_{20}$ Scen 2 (6) *And*	FS ≤ 1.75 m *and* THR_{1200s} ≤ 10 MJ *and* Peak HRR ≤ 20 kW *and* FIGRA ≤ 120 Ws^{-1}	Smoke production (3, 7) and Flaming droplets/particles (4) and Acidity (5)
	EN 50265-2-1	H ≤ 425 mm	
$B2_{ca}$	$FIPEC_{20}$ Scen 1 (6) *And*	FS ≤ 1.5 m; *and* THR_{1200s} ≤ 15 MJ *and* Peak HRR ≤ 30 kW *and* FIGRA ≤ 150 Ws^{-1}	Smoke production (3, 8) and Flaming droplets/particles (4) and Acidity (5)
	EN 50265-2-1	H ≤ 425 mm	
C_{ca}	$FIPEC_{20}$ Scen 1 (6) *And*	FS ≤ 2.0 m; *and* THR_{1200s} ≤ 30 MJ *and* Peak HRR ≤ 60 kW *and* FIGRA ≤ 300 Ws^{-1}	Smoke production (3, 8) and Flaming droplets/particles (4) and Acidity (5)
	EN 50265-2-1	H ≤ 425 mm	
D_{ca}	$FIPEC_{20}$ Scen 1 (6) *And*	THR_{1200s} ≤ 70 MJ *and* Peak HRR ≤ 400 kW *and* FIGRA ≤ 1300 W/s	Smoke production (3, 8) and Flaming droplets/particles (4) and Acidity (5)
	EN 50265-2-1	H ≤ 425 mm	
E_{ca}	EN 50265-2-1	H ≤ 425 mm	
F_{ca}	No performance determined		

Definition of FIGRA





FIPEC apparatus

2 scenarios

- FIPEC 1:

20,5 kW burner
20 minutes

- FIPEC 2 :

30 kW burner
20 minutes
Backing board

2 cables were tested:

1. cable with jacket based on **ATH**

2. cable with nanocomposite jacket based on **ATH & organoclay**

Technology invented by Kabelwerk EUPEN AG
Review of nanocomposites for the cable industry:
G. Beyer, *Journal of Fire Scienes*, 2005

	NHXMH-J 4 x 16 mm^2 Classical only ATH based jacket	NHXMH-J 4 x 16 mm^2 Nanocomposite based jacket
FIPEC Scenario 1 20,5 kW flame	Flame spread = 49 cm PHRR = 27.1 kW FIGRA = 63.2 W s^{-1}	Flame spread = 48 cm PHRR = 22.9 kW FIGRA = **20.3 W s^{-1}**
FIPEC Scenario 2 30 kW flame & plate Backing board	Flame spread = 185 cm PHRR = 58.6 kW FIGRA = 53.5 W s^{-1}	Flame spread = **121 cm** PHRR = 55.8 kW FIGRA = 47.9 W s^{-1}

Dripping of burning polymer

Non-dripping of burning polymer

Fire test for data cables

IEC 60332-3-25

Tests on electric cables under fire conditions

Test for vertical flame spread of vertically-mounted bunched wires or cables

Category D

Fire test according to IEC 60332-3

FRNH data cable Cat 5 E
4x2xAWG 24/1

FR-trial better for the metal-hydroxide .....

reason ?

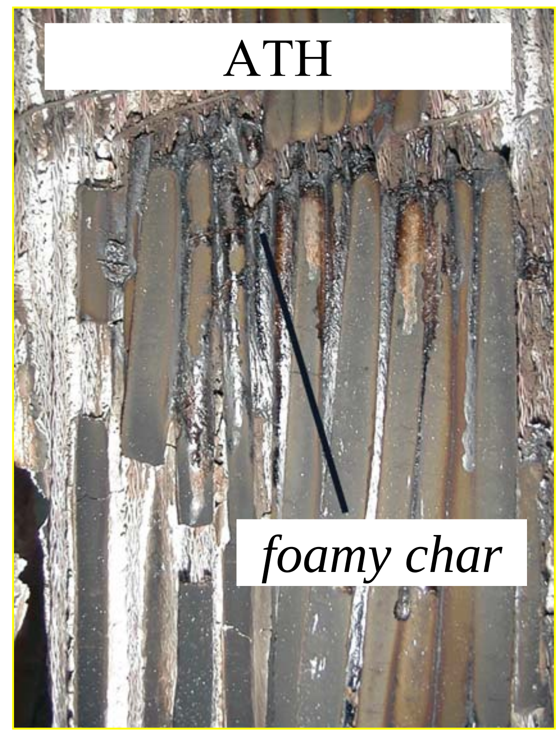
Char aspect of the cable jackets

Nanocomposite	Metal hydroxide
(ATH + organoclay)	ATH
↓	↓
<u>reduced</u> thickness	*<u>increased</u> thickness*
" compact "	*" foamy "*

Char-character of the cable jackets

The nanocomposite outer-sheathes are not forming a complete barrier for the flame of the burner => <u>chemin-effect</u>

The metal-hydroxide outer-sheathes are forming <u>a complete barrier</u> for the flame of the burner



Summary

- FR-function of organoclays is related to the degradation mechanism of the polymer matrix

  2 mechanisms :
  - change of reaction pathways
  - barrier effects

Summary

- **LDH** are reported to be very promising flame retardants
- The strong eletrostatic forces betweel the layers can be problem to disperse them in a proper nano-dimension
- Brabender-mixing chamber is not a sufficient mixing tool for LDH in EVA, LDPE or plasticizied PVC

Summary

- **Nanocomposites** as nanostructured highly ffective flame retardants will give benefits the improved FR-properties as requested by FIPEC-procedure

- sometimes “unusaul” FR-results possible => chemin-effect …..