How to formulate HFFR compounds for cables based on natural magnesium hydroxide (MDH)

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IPOOL srl

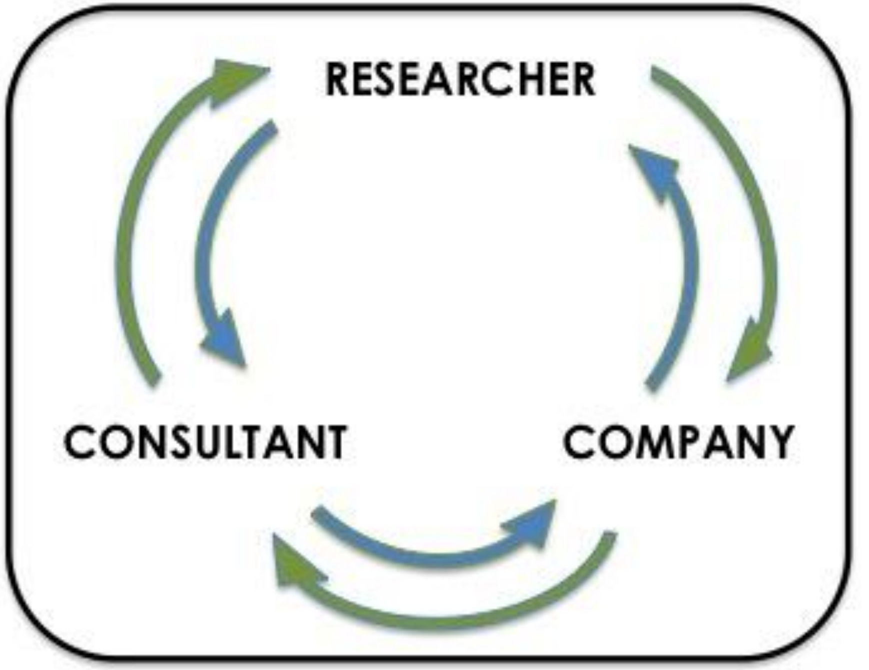
Spin-off company of National Council of Research institute (CNR) of Italy. It has been established in July 2011 and it is founded on the strictly connected work of researchers, professionals and industrial companies.

Mission

Scientific and industrial development of know-how and applications regarding chemical and physical properties of materials and specific measurements methods and instruments.

Technical consulting about design, industrialization, and marketing of raw materials and compounds with
high performances and low environmental impact.

Specialized services of Applicative Research and Technological Development for companies operating in safe-materials (flame retardant and low smokes) and recycling materials (circular economy).

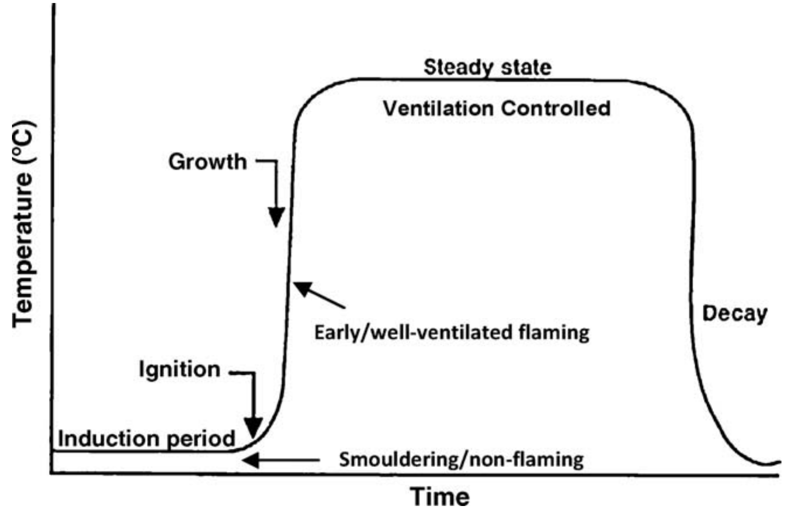


"Safety in case of fire"

- To retard the spread of fire development and the spread of fire and smoke in the work so as to enable occupants near and/or remote from the room of fire to have sufficient time to escape.

- To enable the fire brigade/rescue teams to control the fire before it is too large.

Available Safe Escape Time (ASET) must be greater than ***Required Safe Escape Time*** (RSET) by a margin of safety.

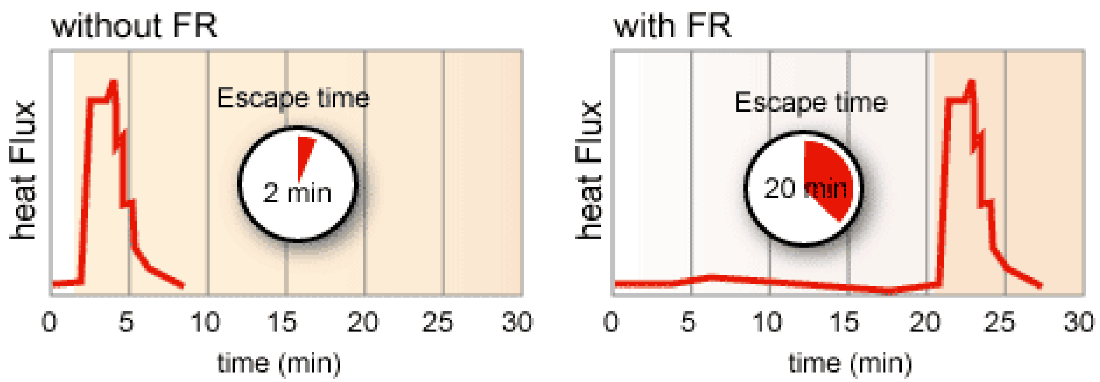


During fires, the acute survival risks are reduced vision caused by **smoke** which greatly increases the time to exit, confusion, panic, loss of orientation, pain and breathing problems caused by irritating products and loss of consciousness caused by asphyxiating gases and burns derived from exposure to radiant and convective heat, which could lead to collapse.

Main compounded materials for cables

Polymers	Insulation	Bedding	Sheathing
XLPE	●		○
EPR/EPDM	●	●	
PVC	●	●	●
Thermoplastic HFFR	●	●	●
XL-HFFR	●		●
CPE	○		●
NBR/PVC			●
TPU			●

- Increasing demand of flame-retardant materials
- Increased role of FR bedding compound (competitive cost, high FR)
- Global competition between halogenated and halogen-free materials



Comparative behaviour of main base polymers in fire

Code	Description	Self-ignition T (°C)	Heat of combustion MJ/kg	LOI (%)	Flame spread	Tendency to drip	Smoke release
EVA/EVM	Poly(ethylene-vinyl acetate)	320	38-42	<20	High	Medium	Medium
EPR/EPDM	Ethylene-Propylene rubber	350	44	<20	High	Medium	Medium
PE/POE/PP	Polyethylene, Polypropylene and related plastomers	350	44	<20	High	High	Medium
CPE	Chlorinated polyethylene	400	30-35	22-24	Low	No	High
PVC	Polyvinyl chloride	450	<20	42	Low	No	High
p-PVC	Plasticised Polyvinyl chloride	250-300	25-30	23	Low	No	High

- Flexible polymers with low crystallinity (and low T_g) could be modified with high loading of flame retardants and smoke suppressants additives and minerals.
- The high content of (highly burnable) plasticiser penalizes behaviour of PVC in fire.
- To guarantee cables pass fire tests, different FR additives, FR minerals and FR synergists are used for the different base polymers.

Why Halogen free?

- Globally growing interest on toxicity and bioaccumulation problems of flame retardants containing halogenated compounds.

- Main reason for fatalities is the emission of dense and poisonous gases like the acid gaseous emissions during combustion in real fires of halogens containing materials synergized with Antimony trioxide

- Corrosive gases damage the concrete reinforcement as well as electronic devices like PCs, alarms, servers, elevators

⇒ Need of NO toxic, no asphyxiant, no acidic, no corrosive, and LOW smoke FR compounds

Why PVC?

"*The question of the importance of smoke toxicity in relation to fire hazard is an open question, and for sure over weighted in Europe... well over 90% of fire deaths are the result of fires becoming too big and thus resulting in too much toxic smoke, whatever are the burning materials generating the smokes… At flashover,* ***every polymer will give off ca. 20% of its weight as CO****: that is toxic enough to be lethal. Toxic potency is a minor contributor to fire hazard and it is most critically dominated by CO concentration. Fire hazard and life safety are best served by ensuring that fires remain small, meaning that they need to exhibit* ***heat release rates as small as possible***"

M.M. Hirschler, *Fire safety, smoke toxicity and acidity*, Proc. Flame Retardants 2004

FR LS PVC in Middle East, Russia and India is widely used, and is growing in those markets as answer of PVC industry to new "*green*" and "*safe*" feeling.

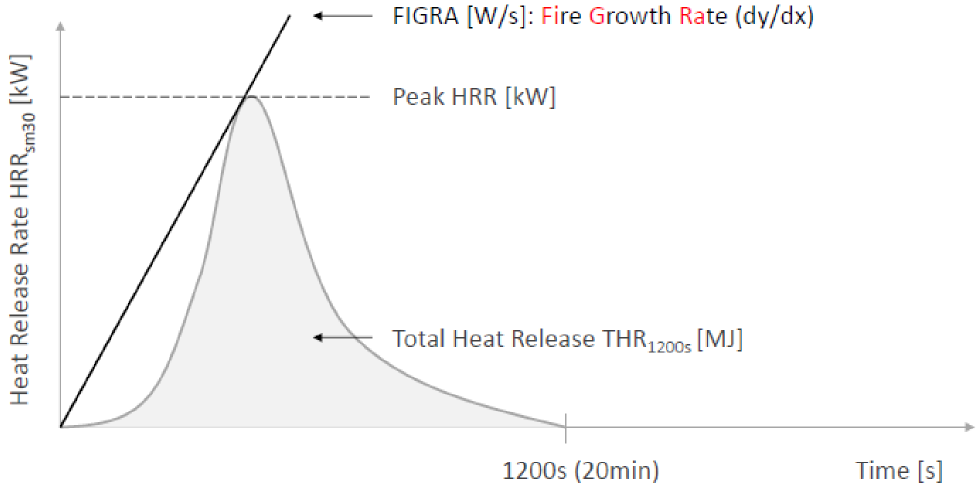
In Europe, the new CPR classification requested for many cable applications is $\mathbf{B2_{ca}\ d_0}$ which is relatively easy for PVC cables due to intrinsically not dripping behaviour and the very low heat of combustion (=low HRR).

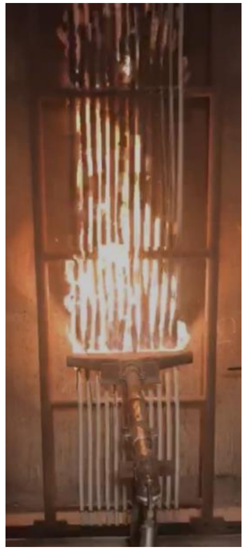
Aluminum and magnesium hydroxides, phosphorous based plasticisers, tin and zinc compounds, natural magnesium minerals, fibrillar silicate (sepiolite) and nano-silica,….

→ **Many solutions available for fire safe and cost competitive PVC cables**

Fire test on cables – test EN 50399 (CPR)

Measure	Aim
FS [m]	Main class
TH1200S [MJ]	Main class
Peak HRR [kW]	Main class
FIGRAO, 4MJ, [W/s]	Main class
Peak SPR [m2/s]	S1, S2, S3
TSP1200s [m2]	S1, S2, S3
Flaming droplets (Y/N)	d0, d1 d2





Main issues since introduction of CPR:

- Increased content of mineral fillers ⇒ increased viscosity and density
  reduced mechanical properties and flexibility
  reduced resistance to ageing test in air, water and oil
- Even with excellent results in heat release and burned length, sometime very difficult to have classification **d_0** (*no droplets or not burning droplets*) or **d_1** (*fast self-extinguish droplets*) due to frequent use of silane XLPE as insulation.

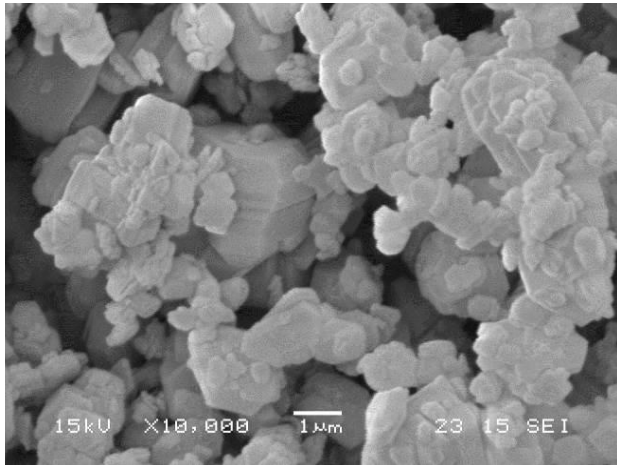
⇒ ***New technical paradigm, chance for market evolution***

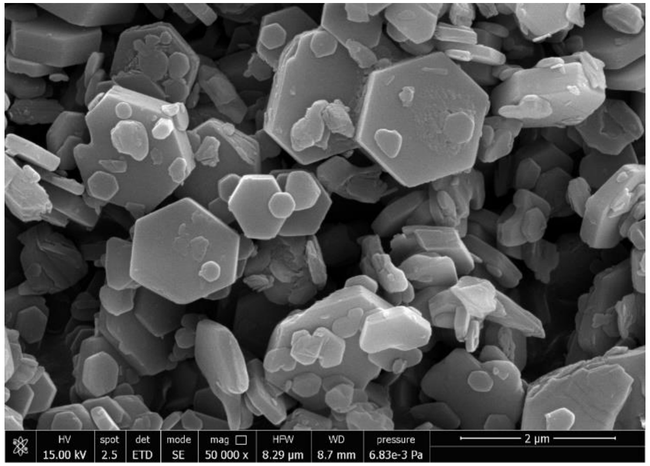
Evolution of HFFR compounds – Milestones/1

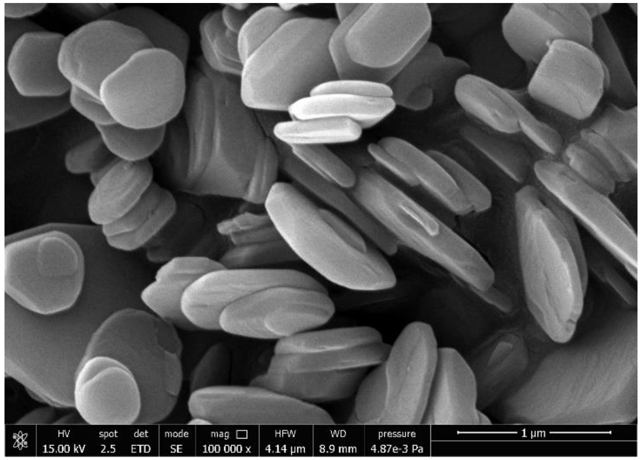
1st generation - 1980-2000, only fine synthetic FR fillers, 60-62% dosage on low MFI EVA

Base polymers	Coupling agents	Main FR filler	Filler partners	Additives
EVA18, EVA 28 MFI<3.0	AMEO	Fine pp ATH	Fine pp MDH	Antiox, Stabilisers
LLDPE MFI=1	VTMS+peroxide	Fine pp MDH		

- Niche market, expensive formulations, low processing speed





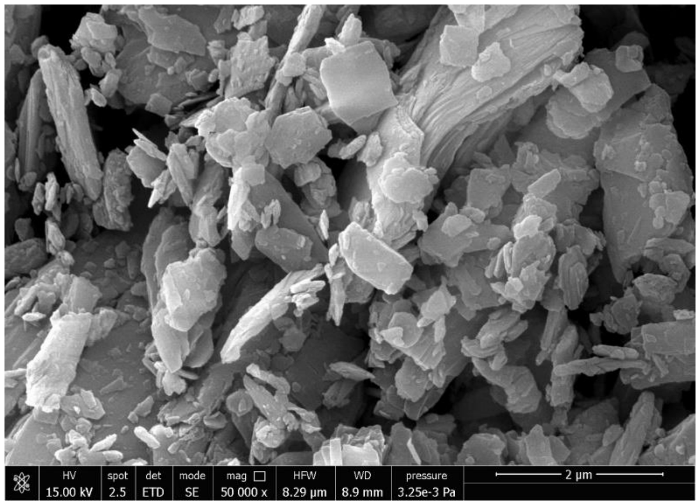


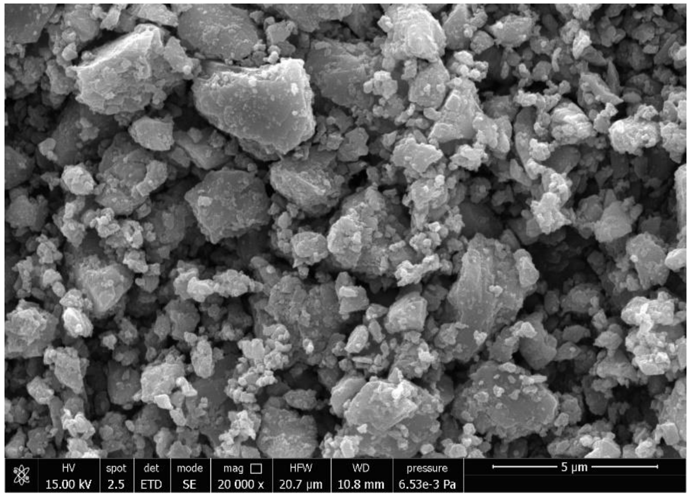
Evolution of HFFR compounds – Milestones/2

2nd generation: 2000 till now, maleated coupling, also milled FR fillers, till 65% loading on EVA+POE

Base polymers	Coupling agent	Main FR fillers	Filler partners	Additives
EVA28 MFI=3-7	LLDPE-g-MAH	Fine pp ATH	Fine Milled ATH	Antiox, Stabilisers
LLDPE MFI=3-6		Fine pp MDH	**Milled $CaCO_3$**	Silicon lubricants
C_2-C_8 Plastomers		**Milled n-MDH**		

- Combination of pp-ATH with milled natural MDH (n-MDH) for high FR applications
- Combination of pp-ATH with $CaCO_3$ for high speed and competitive formulations
- First cable compounds based on POE+n-MDH based (ATH-free and EVA-free)
- Focus: low cost and high production speed as PVC



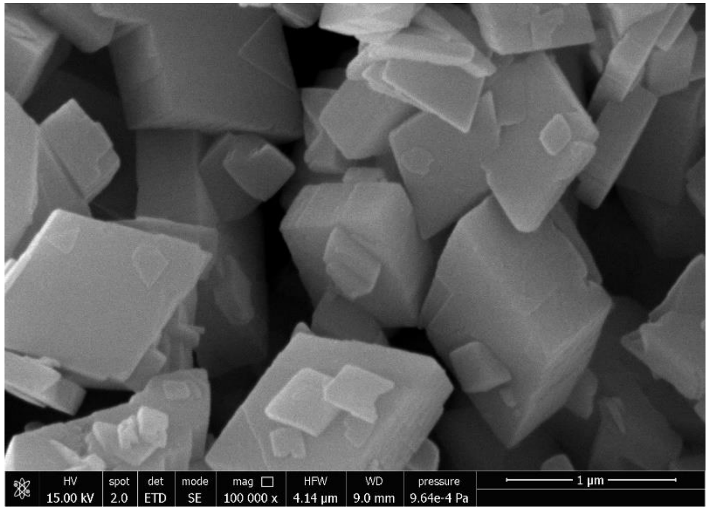


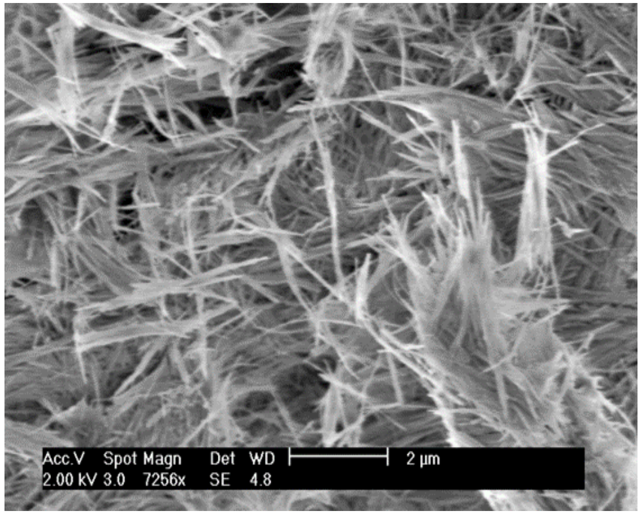
Evolution of HFFR compounds – Milestones/3

3rd generation (CPR): 2017- today, Combination of few fillers and FR synergist to comply with CPR.

Base polymers	Coupling agents	Main FR filler	Filler partners	FR synergists	Additives
EVA28 MFI=3-7	LLDPE-g-MAH	Fine pp ATH	Milled n-MDH	Nanoclay	Antiox, Stabilisers
LLDPE MFI=3-6	POE-g-MAH	Fine pp MDH	Milled $CaCO_3$	**Mg silicate**	Silicon lubricants
C_2-C_8 Plastomers	VTMS+peroxide	Milled n-MDH	**Böhmite**	Silica	Hydrophobic agent
C_3-C_2 Plastomers				P-red	Polar wax

- Higher filler loading, with combined couplings and new high performance plastomers
- Antidripping and char forming agents for d_0
- Significant increase of use of n-MDH (brucite)





Typical composition of HFFR cable compound (EVA+ATH)

Component	%	Notes
EVA18 + EVA28	18-22	Polar, flexible polyolefin
C_2-C_8 Plastomer	4 - 8	Non polar, flexible polymer
mLLDPE	4 - 8	Non polar, rigid polymer
Coupling agent		
LLDPE-g-MAH	4 - 5	Maleated coupling agent
Fillers (total=62-65%)		
Main FR filler	45-65	Fine precipitate ATH
2^{nd} FR filler	0-15	Stearic coated n-MDH d_{50}=3.5 μm (Ecopiren 3.5C)
3^{rd} filler	0-10	Stearic coated $CaCO_3$ d_{50}=1.5 μm
Additives		
Silicon masterbatch	1	External lubricant (Silmaprocess AQ2567)
Hydrophobic agent	0,5	Silan masterbatch in pellets (Silmastab AX2244)
Stabilizer	0,5	Blend of stabilizers/antioxidants (Silmastab AE1527E)

⇒ Best performances in fire test are with n-MDH and without $CaCO_3$

Vertical burning behaviour


Mini-SBI corner test on HFFR compound based only on EVA+ATH

Mini-SBI corner test on HFFR compound based on EVA+ATH+n-MDH or EVA+ATH+antidripping synergyst


POE+n-MDH composition of HFFR cable compound

Component	%	Notes
C_2-C_8 Plastomer	10 -15	Polar, flexible polyolefin
C_3-C_2 Plastomer	10 -15	Polar, flexible polyolefin, high melting point
Fillers (total=60-65%)		
Main FR filler	55 - 60	milled n-MDH d_{50}=3.5 μm (Ecopiren 3.5C)
2nd FR filler	0 - 5	$CaCO_3$ or Böhmite (Aluprem SR 100 MES)
FR synergist	3	Coated Mg silicate (Adins Clay Sil-1)
Coupling agents		
POE-g-MAH	1-3	Maleated coupling agent
Silan coupling agent	1.5	Silan+perox in pellets (Silmalink AX2292P)
Stabilizer/lubricants		
Polar wax	2	Dispersing/wetting agent (Viscospeed)
Silicon Masterbatch	1.5	External lubricant (Silmaprocess AQ2567)
Stabilizer	0.5	Blend of stabilizers/antioxidants (Silmastab AE1527E)

⇒ ***Good Mechanical properties are due to plastomers and maleated+silan couplings***
⇒ ***Perfect dispersion of n-MDH and Sepiolite comes from polar-wax***
⇒ ***Compounding/extrusion temperature is till 250°C (420°F) as ingredients thermally very stable***

Mechanical properties and Laboratory scale vertical fire test

PROPERTIES (60% nMDH)	POE+nMDH
Density at 23°C (g/cm^3)	1,453
MFI – 21,6kg @ 190°C (g/10min)	6,6
Tensile Strength (MPa)	14,8
Elongation at break (%)	245
ΔTS after 7dd@100°C in oven	0%
ΔE@B after 7dd@100°C in oven	-10%
ΔTS after 4h@70°C in ASTM 2 oil	-17%
ΔE@B after 4h@70°C in ASTM 2 oil	-3%
ΔTS after 7dd@70°C in water	-18%
ΔE@B after 7dd@70°C in water	29%
Water absorbtion	0,40%

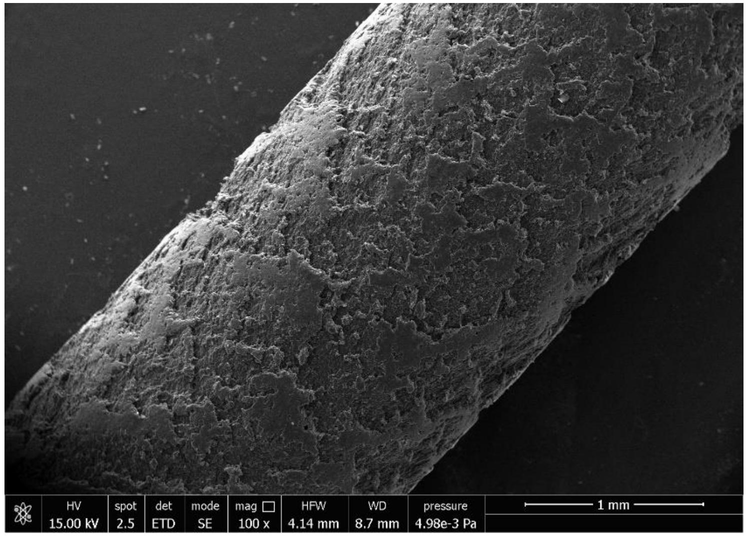
Excellent mechanical properties, before and after ageing tests in different conditions.
Medium flame retardancy due to easy dripping and relatively low filler loading

How to improve:

- + 2% Viscospeed (polar wax)
- + 3% Adins Clay SIL-1 (Mg silicate)
- + 4% Masteret 40460 (Red P MB)

One or more of above actions

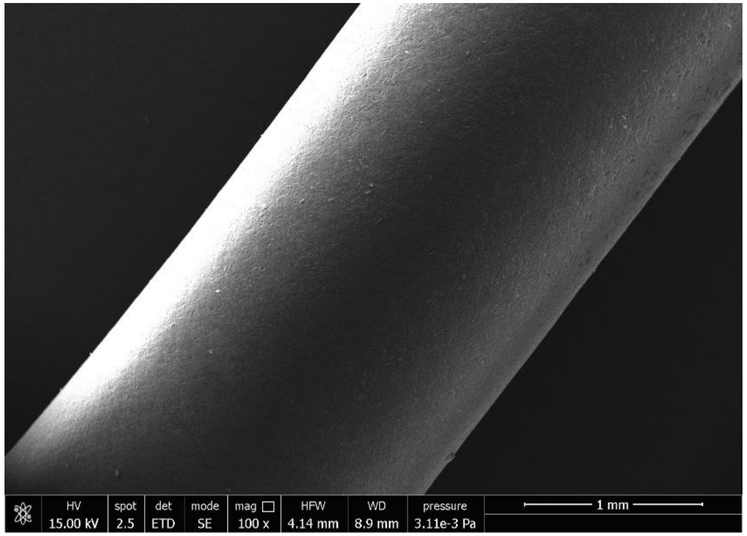
Surface quality of POE+n-MDH cable compounds



No problems for big cables extruded till 20-30 m/min
Roughness for line speed >50 m/min

- Reduce speed of production
- Reduce total filler loading
- Addition of polypropylene

- Smaller+longer die (=increase compression)
- Lower T in the head/die
- 5 – 10% Bohmite (Aluprem SR 100 MES)
- 5 – 10% fine pp MDH
- 1 – 2% Silicon gum MB



One or more of above actions

Competition between halogen free and PVC compounds in cables

(standard building wire application)

Name	FR PVC	FR LS PVC	Next FR LS PVC	HFFR	CPR grade HFFR	Next CPR Grade HFFR
LOI	28-32	34-38	34-38	32-36	38-42	38-42
Specific gravity	1.52	1.55	1.55	1.48-1.52	>1.54	1.48-1.52
Extrusion speed	High	Medium	High	Medium	Low	Medium
Electrical properties	Medium	Medium	Medium	High	High	High
Smoke emission	High	Medium	Low	Low	Low	Low
Smoke acidity	High	Medium	Low	Low	Low	Low
Dripping	No	No	No	Yes	No	No
Typical CPR target	$B2_{ca}\ s_3\ d_0\ a_3$	$B2_{ca}\ s_2\ d_0\ a_3$	$B2_{ca}\ s_2\ d_0\ a_3$	$D_{ca}\ s_1\ d_2\ a_1$	$C_{ca}\ s_1\ d_1\ a_1$	$B2_{ca}\ s_1\ d_0\ a_1$
Relative price	1.0	1.1	?	1.3	1.7	?

⇒ ***Intense technical and commercial competition, globally beneficial for safety and environment***

Conclusions

- **Natural MDH**, when properly selected with high purity, low iron content, low silicate contents, and carefully processed to d_{50}=3-5 microns, shows same flame retardant and smoke suppressant performances of synthetic MDH, in PVC as well as in polyolefins.

- Globally growing use of high quality natural milled MDH in PVC compounds as well as in HFFR compounds allowed to improve flame retardancy of cables (heat release, smoke emission, toxicity, no-dripping), as well as the competitiveness.

- In HFFR compounds, the actually most used formulation for high FR are based on EVA+pp-ATH+n-MDH, and R&D activity is focused to move to POE+n-MDH formulations by taking advantage from high performances of **new metallocenic copolymers** (C_2-C_8, C_3-C_2), and new additives for dispersion (**polar waxes**), lubrication (**silicon MB**), hydrophobicity (**silan MB**), surface smoothness (**Böhmite**) and antidripping (**coated sepiolite**).

- Evolution of PVC compounds and HFFR compounds gives many opportunities to cable manufactures to design more competitive and more fire-safe cables.

Raw materials supplied by:

www.torminerals.com, producer of high purity, extra-white ATH and Böhmite.

www.italmatch.com, producer of special phosphorous-based flame retardant for polypropylene, polyurethane, polyamide, HFFR and PVC compounds.

www.silmaster.com, producer of special masterbatches for HFFR compounds (silicon, silane, antiox/stabs)

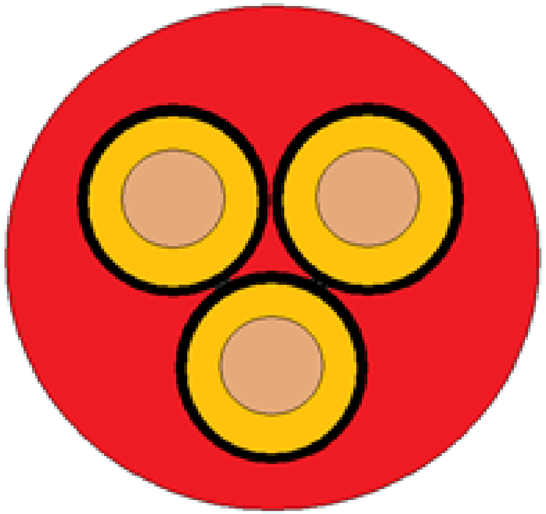
www.europiren.com, producer of high quality, high purity, fine milled, natural magnesium hydroxide.

www.tolsa.com, producer of inorganic antidripping and ceramifying FR synergist for HFFR and PVC compounds

www.innospec.com, producer of special polar waxes and polymers

Thank you for the kind attention!

Questions are welcome



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Presentation available upon request