POLYMERS IN CABLES 2018

Philadelphia, Pennsylvania, USA

« Mineral and polymeric additives as new synergist for HFFR compounds»

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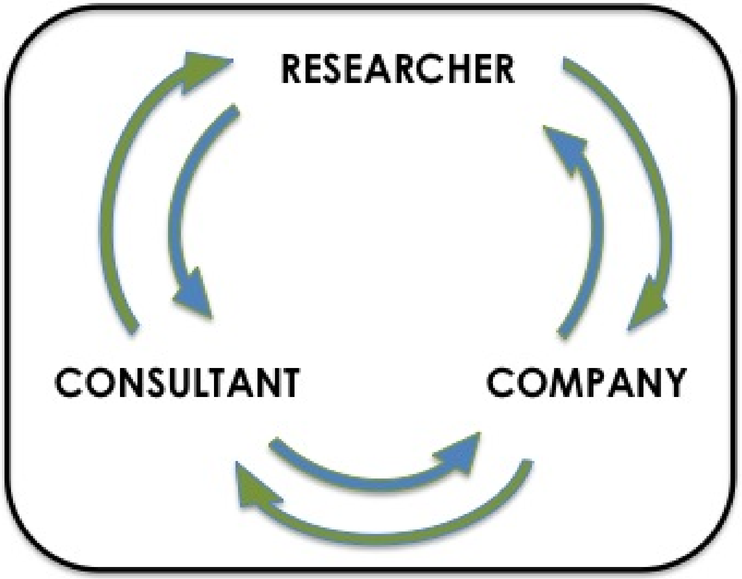
IPool is a spin-off company of National Council of Research institute (CNR) in Pisa. It has been established in July 2011 and it is founded on the strictly connected work of researchers, professionals and industrial companies.

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 materials recycling (circular economy).

Evolution of Flame Retardant Halogen Free compounds

Synonymous: HFFR – LSZH – LS0H compounds

1980-2000	Birth and first development	EVA/PE + fine pp ATH and/or fine pp MDH + silan coupling agent
2000-2010	Fast growth and diffusion in Europe	EVA/PE/POE + *pp*-ATH + ground *n*-MDH + PE-g-MAH coupling agent POE/PP + ground *n*-MDH PP + coated *pp*-MDH (for automotive)
Since 2010	Diffusion in Middle East / Asia	Improved compounds for high crack resistance cables in harsh environments
Since 2016	New CPR in Europe with EN 50399 fire classification	Improved compounds for higher flame-retardant classification of cables with low and no-acidic smokes, no dripping and char cohesion. Development of highly FR bedding compounds

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Components of HFFR polyolefin compounds for cables

Main Polymers (flexibility and elongation at break)

Polar PE-copolymers: EVA, EMA/EEA/EBA

Non-polar PE-copolymers: POE and ULDPE based on C_2-C_8 or C_2-C_4 copolymers
Flexible PP copolymers
EPR/EPDM

Other Polymers (High melting point and fluidity): LLDPE, metallocene LLDPE, PP rigid copolymers

Main flame retardant fillers

Fine precipitated fillers: Aluminum trihydrate (ATH), Magnesium hydroxide (MDH)
Ground fillers: coarse ATH, natural MDH (brucite), Huntite/Hydromagnesite

Other fillers (synergists): Fine pp Aluminum monohydrate (Böhmite), $CaCO_3$, $MgCO_3$, Zinc borate, nanofillers

Coupling agents: Maleic anhydride grafted polymers, amino silan, vinyl silan

Lubricants/processing aids: Silicon gum, silicon oil (usually in MB form)

Stabilizers/antioxidants: Hindered phenols, phosphites, sulfides, metal deactivators.

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Targets of new generations of thermoplastic HFFR compounds for cables

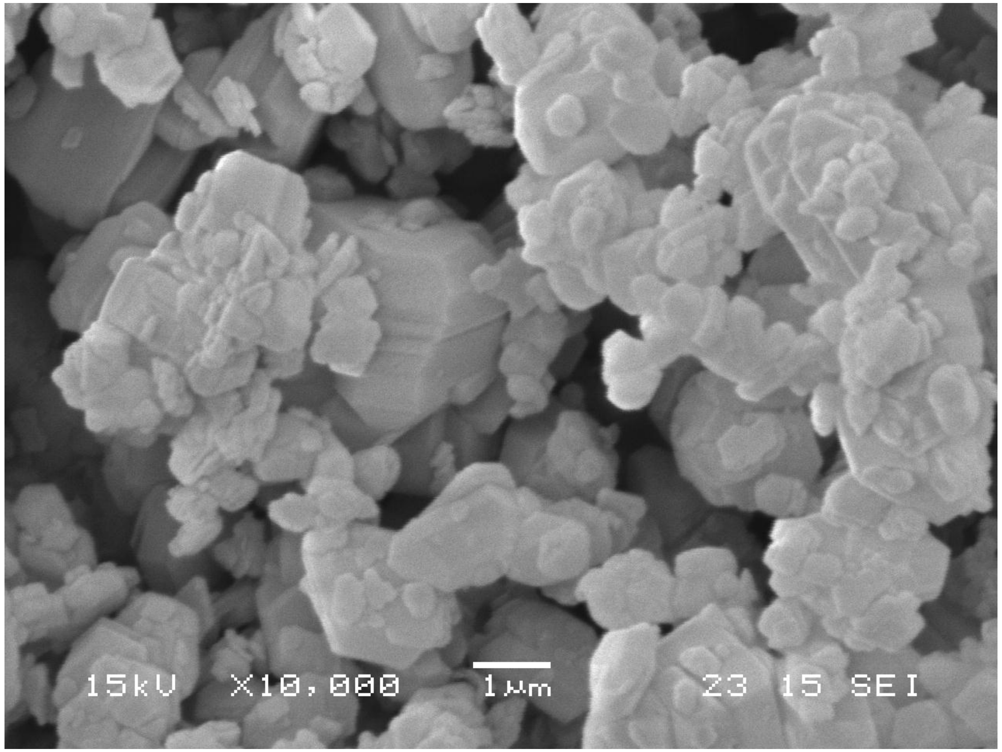
1. High compounding and production speed, as close as possible to PVC compounds

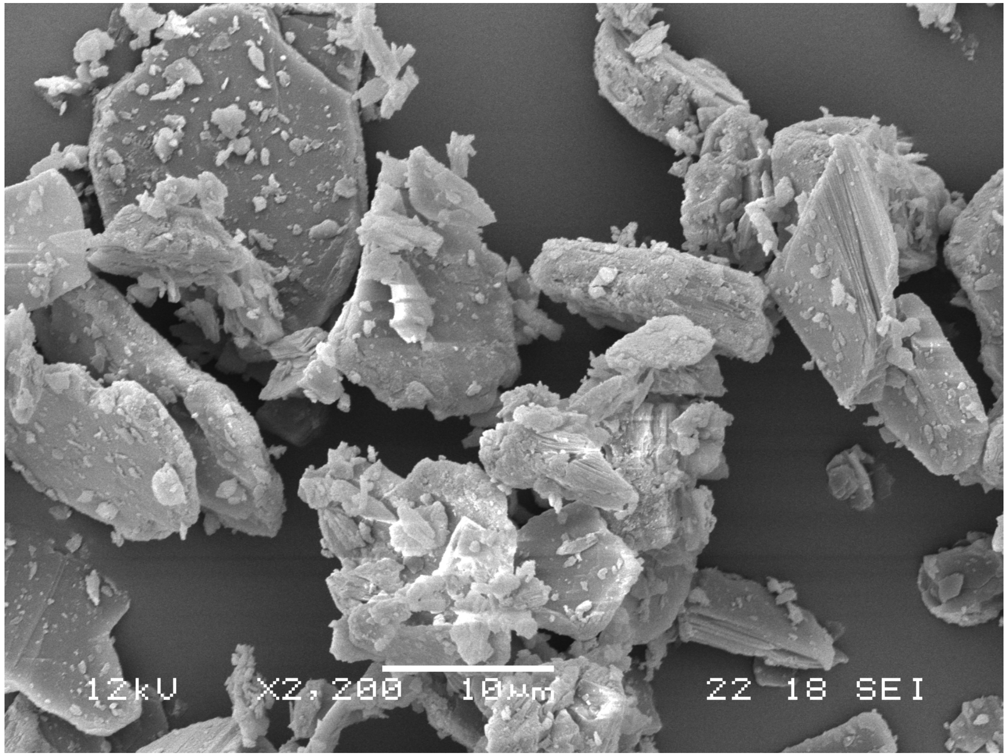
⇒ Low viscosity compounds
⇒ Thermally stable fillers (>200°C)
⇒ Low-hygroscopicity compounds

2. Cost-competitive and <u>sustainable</u> formulations

⇒ Possibility to use wide range of natural and synthetic fillers
⇒ Synergistic combinations

Scanning Electron Microscopy of fine pp-ATH (left) and ground ATH (right)





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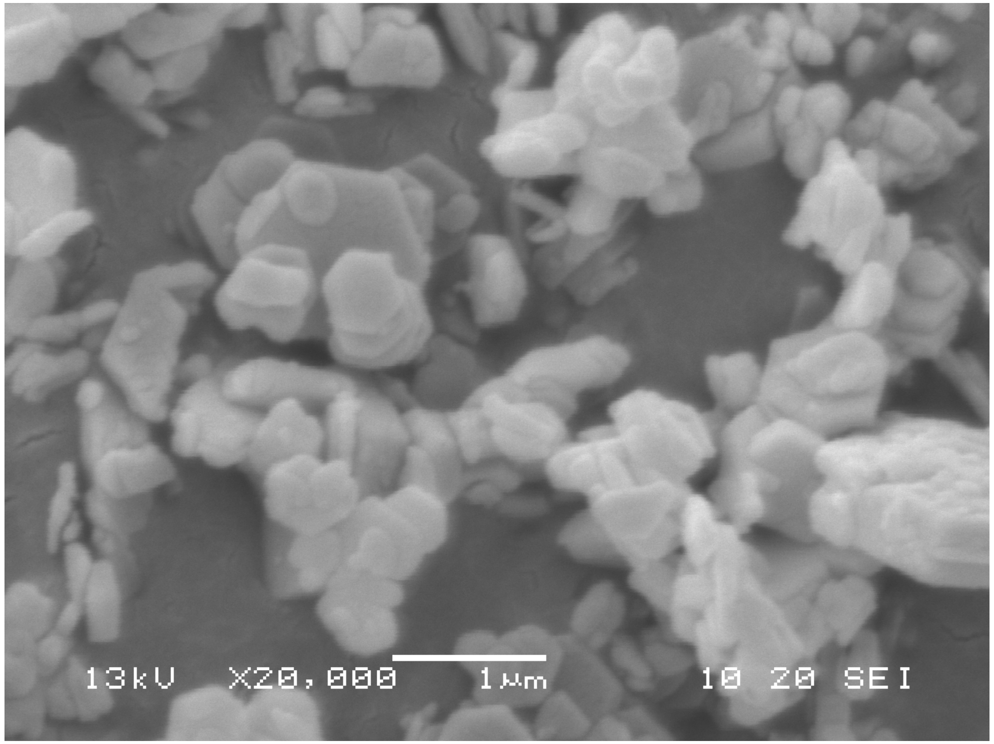
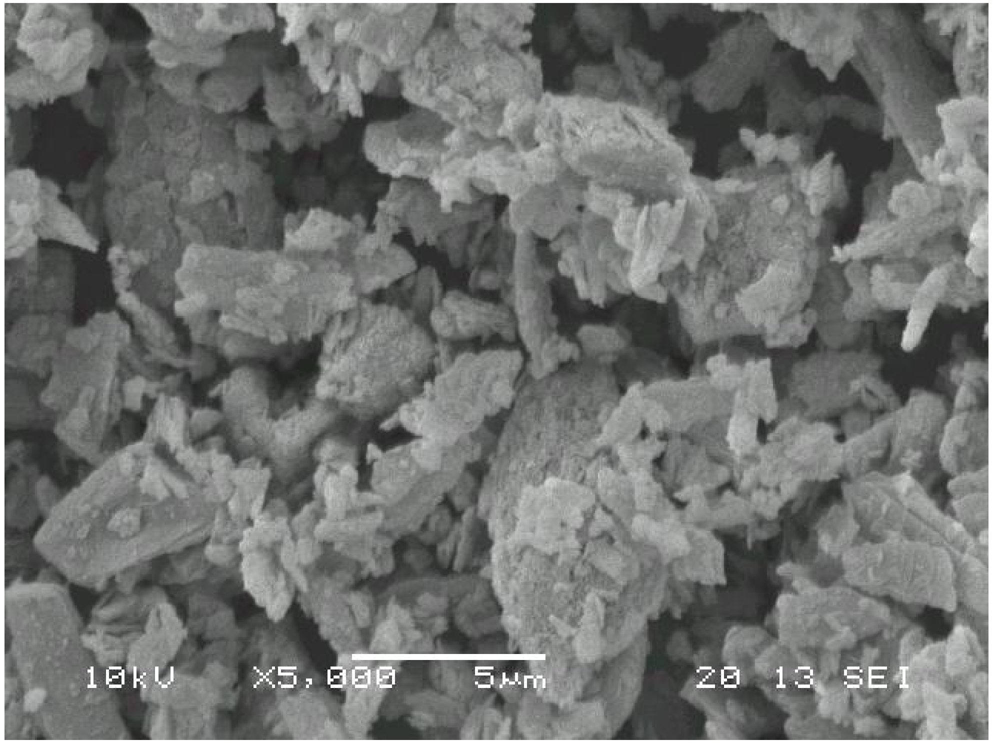
Scanning Electron Microscopy of fine pp-MDH (left) and ground n-MDH (right)





Drawbacks of ground fillers in HFFR compounds vs pp-ATH and pp-MDH

- Lower elongation at break (from 200-250% down to less than 100% in EVA-based compounds)
- Not perfectly smooth surface high speed of extrusion
- Hygroscopicity giving lower electrical properties and potential failure into water immersion tests
- Higher specific surface giving less easy compounding and higher compound viscosity
- Combined effect of high hygroscopicity and high viscosity could create some porosity into extruded cables due to water release and high shear into extruder.
- Off white / light grey colour

⇒ *How to take advantage from the good flame retardancy, the competitive cost and the great availability of ground n-MDH?*

Solution #1 to use *n*-MDH: partial replacement of pp-ATH

(well established solution since more than 15 years)

Formulations:

Components	Trade name	Producer	Load, phr	Dosage, %
*m*LLDPE	Exceed 4518	Exxonchemical	10	3.75
EVA 18% MFI=0.5	Elvax 470	Du Pont	40	15
EVA 28% MFI=3	Elvax 265	Du Pont	40	15
LLDPE-g-MAH	Compoline CO/LL	Auserpolimeri	10	3.75
pp-ATH	Apyral 40CD	Nabaltec	120 – 160	45 - 60
n-MDH	Ecopiren 3.5 or 3.5C	Europiren	0 – 40	0 - 15
Silicon MB	Silmaprocess AL1142A	Silmaster	4	1.5
Hydrophobic MB	Silmastab AX2244	Silmaster	2	0.75
Antioxidant/Stabilizer	Silmastab AE1527	Silmaster	1	0.375

Compounding conditions:

- in co-rotating twin screw extruder at 250 rpm, melt temperature 180-190°C
- in co-kneader single screw extruder at 350 rpm, melt temperature 170-180°C
- in internal mixer, melt temperature 160-170°C and granulation at 150°C

Compounds properties:

Properties	160 phr ATH	120 phr ATH 40 phr Ecopiren® 3,5	100 phr ATH 50 phr Ecopiren® 3,5C
Density at 23°C (g/cm³)	1,47	1,47	1,47
Limited Oxygen Index LOI (%O2)	34	36	35
MFI 21.6kg@190°C (g/10')	15	10	10
Mooney (1+4)@140°C	36	40	38
White Index	88	82	85
Tensile strength at break (MPa)	11,0	12,5	11,0
Elongation at break (%)	220	170	200
ΔTS after 168h@110°C in oven	+10%	+5%	+15%
ΔE@B after 168h@110°C in oven	-15%	-20%	-10%
ΔTS after 4h@80°C in IRM902 oil	-20%	-25%	-15%
ΔE@B 4h@80°C in IRM902 oil	+10%	+5%	+15%
ΔTS after 168h@70°C in water	-10%	-10%	-5%
ΔE@B after 168h@70°C in water	+20%	+25%	+15%
Water absorption, 168h@70°C	0,5%	0,7%	0,6%

⇒ ***No significant effects on overall properties, but FR improvement and cost saving***

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Vertical Burning Test of *pp*ATH+EVA based compound

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Vertical Burning Test of combination *pp*ATH + *n*MDH EVA-based compound

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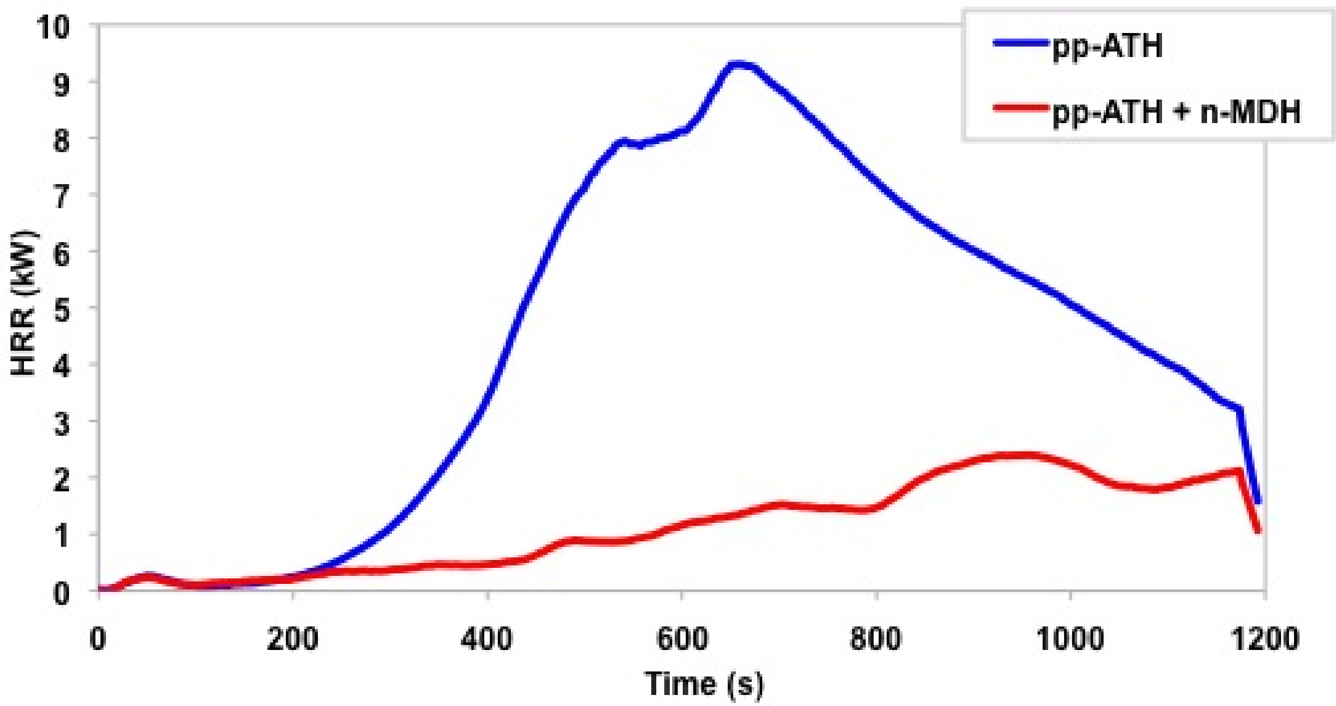
HRR of vertical burning test of HFFR compounds based on *pp*-ATH and *pp*-ATH + *n*-MDH



Solution #2: *n*-MDH in ATH-free POE-based compounds

Formulations:

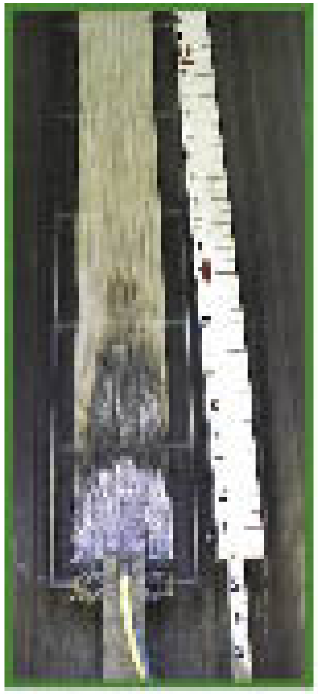
Components	Trade name	Producer	Load, phr	Dosage, %
*m*LLDPE	Exceed 4518	Exxonchemical	26	8
POE	Lucene LC170	LG Chem	58	18
LLDPE-g-MAH	Compoline CO/LL	Auserpolimeri	16	5
n-MDH *	Ecopiren 3.5 or 3.5C or 3.5NP	Europiren	177	55
Fine pp Böhmite	Aluprem TB dry	Tor Minerals	16	5
Stearic coated CaCO3 d_{50}=1 µm	Omyacarb 95T	Omya	16	5
Silicon MB	Silmaprocess AL1142A	Silmaster	5	1,5
EVA wax	Viscowax 353	Innospec	3	1
Hydrophobic MB	Silmastab AX2244	Silmaster	3	1
Antioxidant/Stabilizer	Silmastab AE1527	Silmaster	2	0,5

Compounding conditions:

- in co-rotating twin screw extruder at 400 rpm, melt temperature 210-220°C
- in co-kneader single screw extruder at 400 rpm, melt temperature 200-210°C
- in internal mixer, melt temperature 180°C and granulation at 160°C
-

Compounds properties:

Properties	Ecopiren® 3,5	Ecopiren® 3,5C	Ecopiren® 3,5NP
Density at 23°C (g/cm³)	1,51	1,50	1,50
Limited Oxygen Index LOI (%O2)	34	33	35
MFI 21.6kg@190°C (g/10')	12	10	15
Tensile strength at break (MPa)	12,0	9,5	13,0
Elongation at break (%)	160	>250	200
ΔTS after 168h@110°C in oven	+20%	-5%	+10%
ΔE@B after 168h@110°C in oven	-20%	-25%	-15%
ΔTS after 168h@70°C in water	-25%	-10%	-5%
ΔE@B after 168h@70°C in water	+25%	+5%	-5%
Water absorption, 168h@70°C	1,1%	0,7%	0,5%



- Very nice electrical properties, even after prolonged immersion in water
- Nice behaviour in vertical fire test on bunched cables
- Nice crack resistance in harsh environment when used as sheathing of big armoured cables

*Ecopiren by Europiren: "3.5C" is coated with stearic acid, "3.5NP" is coated with silan

Solution #3: *n*-MDH in ATH-free EVA-based compounds

Formulations:

Components	Trade name	Producer	Load, phr	Dosage, %
*m*LLDPE	Exceed 4518	Exxonchemical	10	3.75
POE	Lucene LC180	LG Chem	40	15
EVA 28% MFI=3	Elvax 265	Du Pont	40	15
ULDPE-g-MAH	Compoline CO/UL 05	Auserpolimeri	10	3.75
n-MDH	Ecopiren 3.5	Europiren	120 - 160	45 - 60
Fine pp Böhmite	Aluprem TB dry	Tor Minerals	0 - 20	0 - 7.5
Stearic coated CaCO3 d_{50}=1 µm	Omyacarb 95T	Omya	0 - 20	0 - 7.5
Silicon MB	Silmaprocess AL1142A	Silmaster	4	1.5
Hydrophobic MB	Silmastab AX2244	Silmaster	2	0.75
Antioxidant/Stabilizer	Silmastab AE1527	Silmaster	1	0.375

Compounding conditions:

- in co-rotating twin screw extruder at 400 rpm, melt temperature 210-220°C
- in co-kneader single screw extruder at 400 rpm, melt temperature 200-210°C
- in internal mixer, melt temperature 180°C and granulation at 160°C

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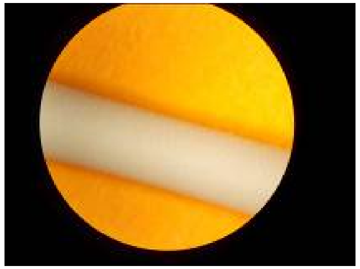
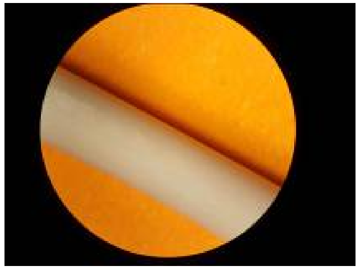
Compounds properties:

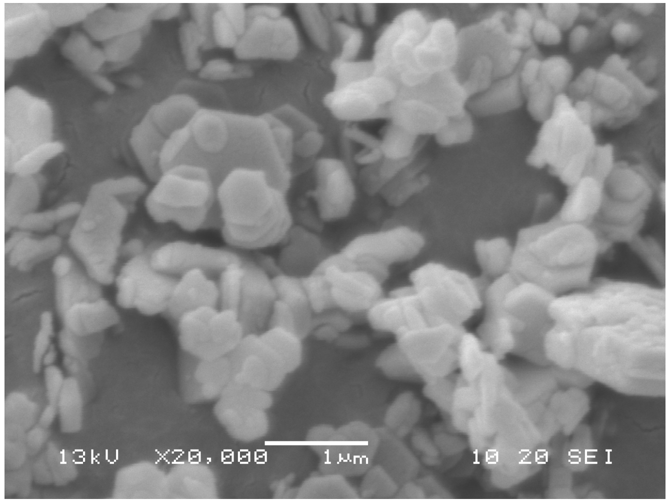


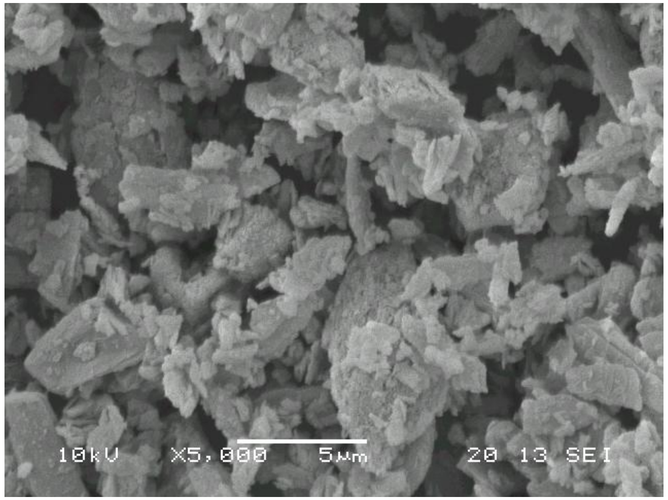

Properties	160 phr *n*-MDH	120 phr *n*-MDH 20 phr Böhmite 20 phr coated CaCO3
Density at 23°C (g/cm^3)	1,47	1.49
Limited Oxygen Index LOI (%O2)	32	34
MFI 21.6kg@190°C (g/10’)	8	12
Mooney (1+4)@140°C	42	37
White Index	79	84
Tensile strength at break (MPa)	13,5	12,0
Elongation at break (%)	140	180
ΔTS after 168h@110°C in oven	+15%	+15%
ΔE@B after 168h@110°C in oven	-20%	-10%
ΔTS after 168h@70°C in water	-20%	-15%
ΔE@B after 168h@70°C in water	+25%	+20%
Water absorption, 168h@70°C	1%	0,8%

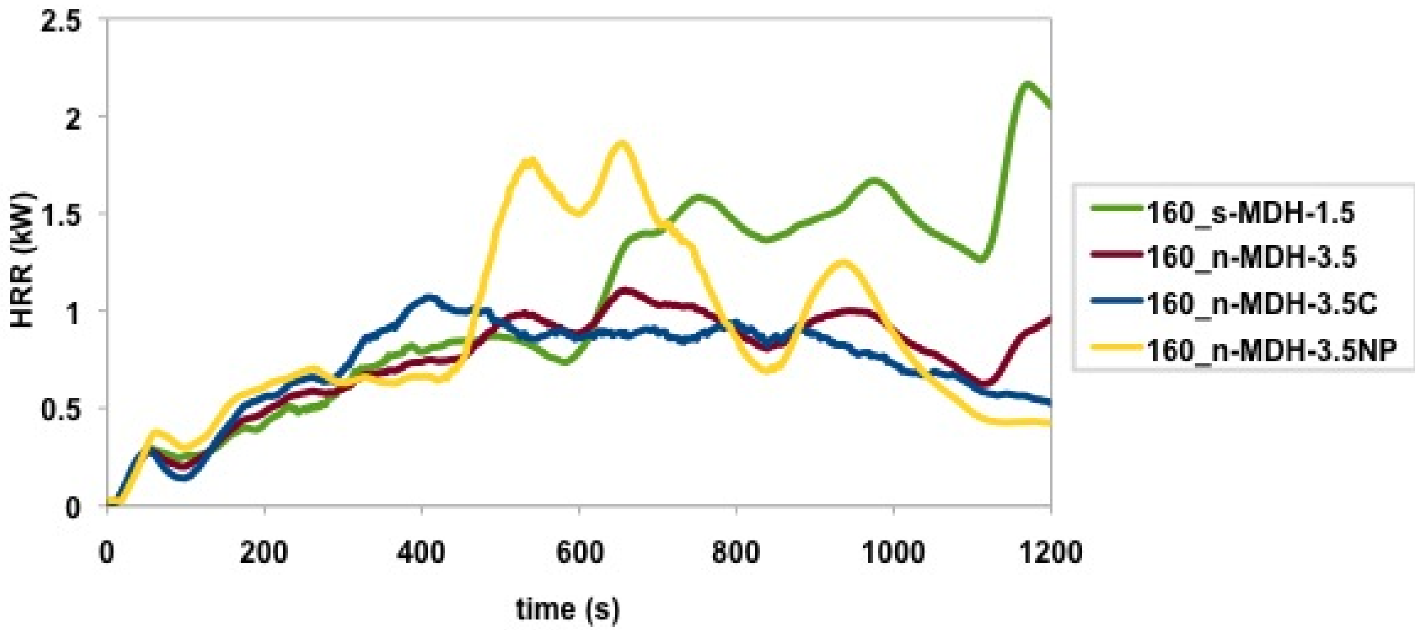



⇒ Introduction of Böhmite reduced viscosity, improved Elongation at break, LOI, colour and surface quality

Flame retardancy: comparison between fine pp synthetic MDH vs natural ground MDH



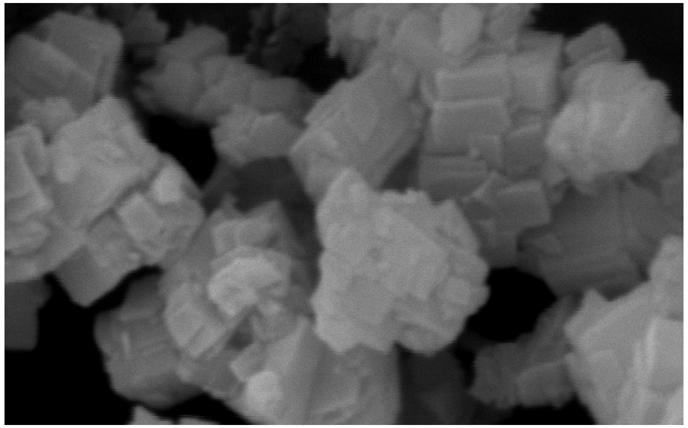


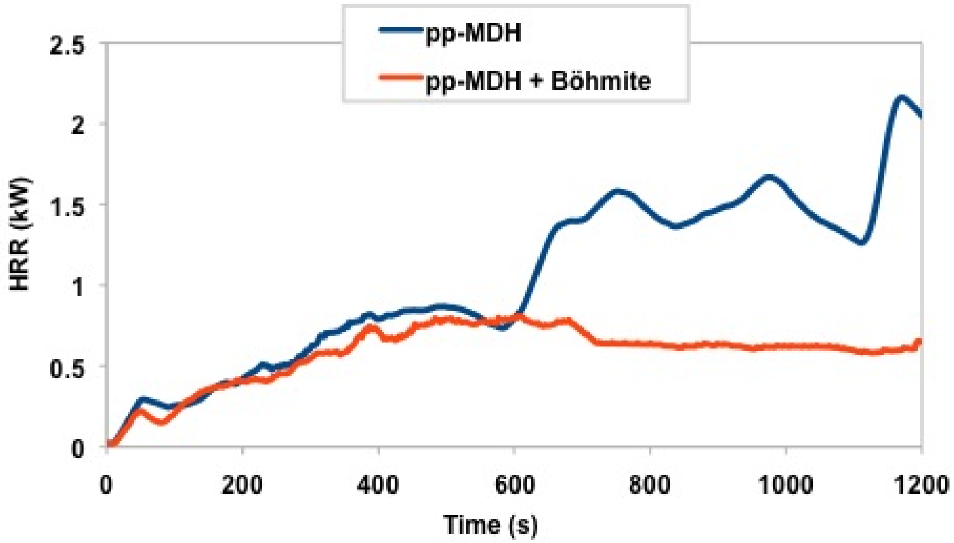


⇒ No relevant differences between synthetic and natural MDH in vertical fire tests in terms of HRR and dripping.

Böhmite synergist filler in HFFR compounds EVA + *pp*-MDH based

Properties	160 phr *pp*-MDH	120 phr *pp*-MDH 40 phr Böhmite
Density at 23°C (g/cm^3)	1,46	1,49
Limited Oxygen Index LOI (%O2)	38	42
MFI 21.6kg@190°C (g/10')	2	6
Mooney (1+4)@140°C	50	45
Tensile strength at break (MPa)	14,0	12,5
Elongation at break (%)	170	200
TS after 168h@110°C in oven	+10%	+5%
E@B after 168h@110°C in oven	-15%	-10%





⇒ Partial replacement of fine pp-MDH with Böhmite* improved rheology, elongation at break and LOI.

*Aluprem TB dry by Tor Minerals

CONCLUSIONS

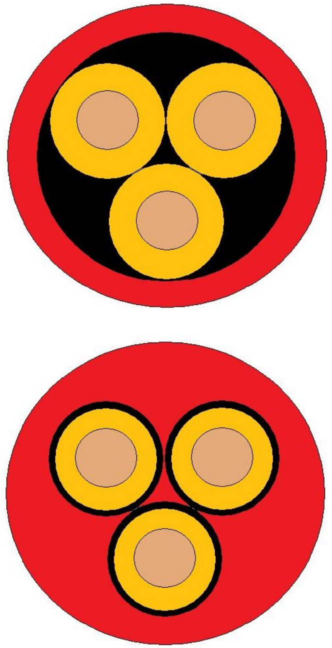
1. Flame retardant fillers are the main components of HFFR compounds for cables, representing 60-65% in weight of typical formulations.

2. New FR regulations, shortage of high quality fine pp-ATH and strong competition in the market push company to introduce ground natural magnesium fillers into HFFR compounds.

3. Thanks to flexible base polymers (like POE, improving E@B), silan-based additives (reducing hygroscopicity), external lubricants (like silicon MB, improving surface quality and reducing viscosity), specific coupling agents (like maleated polyolefins, improving E@B and crack resistance) and non-discolouring stabilizers (improving colour stability), it's nowadays possible for technicians to design recipes with natural ground MDH, with relevant benefits in FR, availability and cost saving.

4. Use of 5-10% of fine precipitated Böhmite in HFFR compounds based on EVA+MDH, improves the overall properties like E@B, rheology, flame retardancy, colour and thermal stability. Böhmite is a mineral additive working with fine *pp*-MDH as well as with ground *n*-MDH.

Thank you for the kind attention!



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