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Optimization of the Mechanical Properties of Polyolefin Composites Loaded with Mineral Fillers for Flame Retardant Cables

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Abstract: Formulations based on mineral fillers and polymeric matrices of different nature were studied to obtain halogen-free flame retardant compounds (HFFR) for cable applications. The work was carried out by comparing fire-retardant mineral fillers of natural origin with synthetic mineral ones available on the market. As a reference, a formulation based on micronized natural magnesium hydroxide (n-MDH, obtained from brucite) and an ethylene-vinyl acetate copolymer with 28% by weight (11% by moles) of vinyl acetate were selected, and the mechanical and flame retardant properties compared with formulations based on secondary polymers combined with EVA, metal hydroxides, and carbonates. Notably, we found a synergistic effect in the mechanical, rheological and flame retardant properties for the composite containing a mixture of n-MDH and boehmite in a 3:1 weight ratio. Overall, the present work provided a complete and optimized recipe for the formulation of polymer composites characterized by the required flame retardant and mechanical features in electric cables applications.

Keywords: halogen-free flame-retardant (HFFR) composites; natural magnesium hydroxide (n-MDH); synthetic magnesium hydroxide (s-MDH); poly (ethylene-co-vinyl acetate) (EVA); ultra-low density polyethylene functionalized whit maleic anhydride (ULDPE-g-MAH); poly (ethylene-co-α-olefin); mechanical properties; LOI

1. Introduction

Since their discovery, mineral fillers have strongly contributed to the growth of the thermoplastic polymers industry. The addition of mineral materials to polymers was initially considered an accessible way of reducing compounds cost, and their utilization as functional additives was proposed only later [1–3]. Nowadays, it is ascertained that fillers enhance specific properties of polymers and for this reason the term *functional filler* has been introduced [4]. There are a lot of fillers used for different applications depending on their functionalities, properties and origin, since their natural or synthetic nature involves different production processes [4–7]. When dispersed in the polymeric composite, their features deeply depend by many characteristics, such as morphology, color, refractive index, presence of impurities, density, hardness, moisture content, thermal stability, modulus, surface chemistry and toxicity [4]. Moreover, the morphology of fillers including particle size, shape, surface area, and particle packing capacity is the key to understanding their

performance in polymers [5–7]. For example, (nano)fillers with very high specific surface area confer composites with remarkable mechanical and gas barrier properties at very low content (<10 wt%) [8], whereas for compounds with flame retardant micronized fillers, such as hydroxides, larger amounts (usually >50 wt%) [9] are required for obtaining an acceptable level of efficiency.

Fillers should only be used in polymers that are chemically compatible and sufficiently amorphous, otherwise the mechanical properties and environmental durability of the material can be severely degraded. In particular, mineral powders blended into the polymer must be uniformly dispersed to ensure consistent flame retardant properties throughout the polymer. Although a high loading of filler is required to display an appreciable improvement of polymer flammability resistance [10], their content could adversely affect other properties, including viscosity increasing and a reduction of the gel time of polymer melts that, in turn, render processing more difficult. Despite these issues, flame retardant fillers are often used because of their wide availability, relatively easy addition into the polymer, and their benefits as smoke and toxicity suppressants. It is important to note that fillers are rarely used alone being instead used in combination with other flame retardants and synergists (such as char forming and antidripping compounds [11]) to achieve a high level of flammability resistance.

Metal hydroxides such as aluminum hydroxide ($Al(OH)_3$, ATH) and magnesium hydroxide ($Mg(OH)_2$, MDH) [5] are the most used family of Halogen-Free Flame Retardants due to several advances [12]: ATH and MDH decompose endothermically at T > 180 °C (Equation (1)) and 330 °C respectively (Equation (2)), with the release of inert gases or vapors, thus resulting in a fire retardancy effect.

$$2\,Al(OH)_3\,(s) \xrightarrow{180-200\,°C} Al_2O_3\,(s) + 3\,H_2O\,(g) \tag{1}$$

$$2\,Mg(OH)_2\,(s) \xrightarrow{330\,°C} 2\,MgO\,(s) + 2\,H_2O\,(g) \tag{2}$$
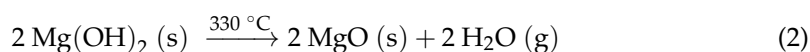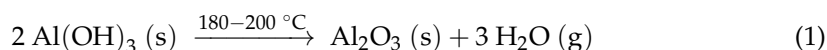
Due to its relatively low decomposition temperature ATH is typically used in poly (vinyl chloride) (PVC), poly (ethylene-vinyl acetate) (EVA), and low density polyethylene (LDPE)-based wire and cable compounds, which have processing temperatures lower than 180 °C [13]. Magnesium hydroxide ($Mg(OH)_2$, MDH) instead is also used in high density polyethylene (HDPE), polypropylene (PP) and polyamide (PA) composites since its decomposition occurs at temperatures around 300 °C [14].

Polyolefins are among the most interesting polymeric matrices for highly filled composites. Notably, composites based on PP and PE and their copolymers offer a variety of uses in different fields of application, i.e., construction, electrical and electronic applications, transportation, etc., and involve different types of functional fillers [15–17].

For the aforementioned characteristics, in the present study, we selected natural milled MDH (n-MDH) from Brucite as flame retardant since it provides the highest performances also in polyolefins matrices (i.e., PP) that require high processing temperatures. Moreover, the great use n-MDH as a flame-retardant filler is mainly due to its competitive cost, its great availability, and its natural origin. Commercial grades are produced by milling processes and supplied by Europiren. For this reason, the particles are irregular and with wider size distribution in comparison with the synthetic ones. Moreover, thanks to careful X-ray separation, n-MDH is obtained with minimized impurities (90–92% MDH) that are attributed to magnesium and calcium carbonates [18]. Even if several papers have tried to correlate filler-matrix interactions with the composite properties and to propose methods for improving them [19,20], just a few of these deal with the use of natural fillers [21,22] due to the difficulty of rationalizing the behavior of the composite system.

Therefore, the challenge of this study was to find the best compromise among the good mechanical performance of the composites, their easy processability and adequate flame retardant characteristics. As reported earlier, the major limitation of HFFRs is their excessive content within the polymer matrix. For this reason, copolymers such as ethylene-co-vinyl acetate (EVA) or ultra-low-density ethylene alpha-olefin copolymers were chosen

as polymeric matrices, since the high amorphous content allows to incorporate large contents of filler [23]. In this direction, it was decided to test formulations as similar as possible to those used in the cable industry, by varying in one case the polymer matrix, i.e., a blend of EVA with 28% by weight (11% by mols) of vinyl acetate comonomer (EVA28) and a polymer that can be PE or PP, and subsequently the type of the mineral filler. EVA28 was chosen because of its particular way of thermal degradation that causes the formation of a protective crust (char) on the cable surface that prevents fire from spreading inwards, thus making EVA one of the most used polymers for the production of cables [24]. EVA is also preferred due to its heat of combustion value equal to 40 KJ/g, which is lower than that of completely apolar polyolefins such as PE (47.74 KJ/g) and PP (45.80 KJ/g). n-MDH was selected in combination with other natural or synthetic fillers, such as synthetic magnesium hydroxide or huntite or bohmite or calcium carbonate, for the identification of the best trade-off between composite flame retardant properties, mechanical performances and processability. Notably, each composite was prepared via a twin-roll mixer and characterized in terms of mechanical (tensile), flame retardant (LOI) and rheological (MFI) properties. The mineral fillers were also characterized by SEM and XRD analyses.

2. Materials and Methods

The raw materials used for the experiments were:

- Poly (ethylene-co-vinyl acetate) EVA28 ELVAX 265A, Du Pont, containing 28 wt.% of vinyl acetate, Melt Flow Index = 3 g/10 min, Density = 0.955 g/cm^3.
- ULDPE-g-MAH, Fusabond N525, Dow, Ultra Low Density Polyethylene C2-C8 Copolymer, grafted with Maleic Anhydride (0.7–1.1 wt.%), Melt Flow Index = 3.7 g/10 min, Density = 0.88 g/cm^3.
- Masterbatch of PDMS, Silmaprocess AL1142A by Silma Srl (Bologna, Italy), composed by 50 wt.% of high viscosity PMDS and 50 wt.% LLDPE, Silicon MB.
- Fillers used are described in Table 1:
- Grades of poly (ethylene-co-α-olefin) used are described in Table 2:
- Grades of C$_3$-C$_2$ copolymers (propylene-rich) used are described in Table 3:

Table 1. Type of fillers used in this work.

Ingredient	Chemical Formula	Origin	Trade Name	Supplier	D_{50} *1 (μm)	BET *2 (m²/g)
n-MDH	Mg(OH)$_2$	Natural	Ecopiren 3.5	Europiren	3.43	11–13
CaCO$_3$ stearic coated	CaCO$_3$	Natural	Polyplex 0	Calcit	2.10	9.5
Boehmite	AlO(OH)	Synthetic	Aluprem TB 1/T	Tor Minerals	1.21	12
S–MDH	Mg(OH)$_2$	Synthetic	Magnifin H5	Huber	1.50	4–6
Mg (OH)$_2$ coated with silane	Mg(OH)$_2$	Synthetic	Magnifin H5GV	Huber	1.50	2–5
coated with stearic acid	Mg(OH)$_2$	Synthetic	Kisuma 5A	Kisuma	1.50	4–7
CaCO$_3$	CaCO$_3$	Synthetic	Winnofil S	Solvay	0.3	14–16
Huntite	CaMg$_3$(CO$_3$)$_4$	Natural	Portafill H5	Sibelco	3.27	18

*1 D_{50}: The portions of particles with diameters smaller and larger than this value are 50%. Also known as the median diameter. Measured by laser diffraction method according to ISO 13320. *2 BET: Determination of the overall specific external and internal surface area of disperse or porous solids measuring the amount of physically adsorbed gas (N$_2$) according to ISO 9277. From TDS.

Table 2. Grades of Poly(ethylene-co-α-olefin) used in this work.

Ingredient [*3]	Trade Name	Supplier	Density [*1]	MFI [*2]	Catalysis
C_4–LLDPE	Flexirene CL10U	Versalis	0.918	2.5	Z-N
C_6–mLLDPE	Exceed 3518	ExxonMobil	0.918	3.5	metallocene
C_6–mLLDPE	Exceed 3812	ExxonMobil	0.912	3.8	metallocene
C_6–mLLDPE	Evolue SP1071C	Prime Polymer	0.910	10	metallocene
C_6–mLLDPE	Exceed 0015XC	ExxonMobil	0.918	15	metallocene
C_8-ULDPE	Engage 8450	Dow	0.902	3	metallocene
C_4-VLDPE	Clearflex MBQ0	Versalis	0.911	13	Z-N

[*1] ASTM D792/ASTM D1505 (g/cm^3), [*2] MFI (2.16 kg @ 190 °C) ASTM D1238/ISO 1133 (g/10 min), [*3] C_4-VLDPE = Very Low Density Polyethylene (comonomer butene), C_4-LLDPE = Low Linear Density Polyethylene (comonomer butene), C_8-ULDPE = Ultra Low Density Polyethylene (comonomer octene), C_6-mLLDPE = metallocenic Linear Low Density Polyethylene (comonomer 1-hexene).

Table 3. Grades of C_3-C_2 copolymers used in this work.

Ingredient	Trade Name	Supplier	Density [*1]	MFI [*2]	Catalysis
Heterophasic PP-EPR	Hifax CA10A	Lyndell-Basell	0.880	0.6	Z-N
C_3–C_2 copolymer	Vistamaxx 6202	Exxon-Mobil	0.862	9.1	metallocene
C_3–C_2 copolymer	Versify 3000	Dow	0.891	8	metallocene

[*1] ASTM D792/ASTM D1505, [*2] MFI (2.16 kg @ 190 °C) ASTM D1238/ISO 1133.

All the composites were prepared via a twin-roll mixer with 45 cm × 15 cm diameter roll (calender) at the constant maximum temperature of 140 °C for 10 min. At first, the polymer matrix was melted for 1 min and then the fillers and additives were added as a mixture. After mixing, composites with a thickness of 1.5 mm were recovered.

Specific gravity is a measure of the ratio of mass of a given volume of material at 23 °C to the same volume of deionized water. The specimen is weighed in air then when immersed in distilled water at 23 °C using a sinker and wire to hold the specimen completely submerged. For each formulation, the density was measured according to the standard ASTM D792 and compared with the calculated value to ensure that the formulation was properly prepared.

The tensile properties were measured with a Tinius Olsen H10KT dynamometer using an elongation speed of 250 mm/min at room temperature. The width and thickness of the specimens were respectively 3.0 mm and 2.0 mm ± 0.2 mm, and the stretched length was 20 mm ± 0.5 mm (according to the standard ISO 37 type 2).

The flow properties were measured using a Melt Flow Index (MFI) instrument according to the standard ISO 1133:1.

The particle morphology of the fillers was evaluated using scanning electron microscopy (SEM) using a FEI Quanta 450 ESEM FEG.

The particle size distribution of the fillers (D_{50}) was evaluated using a laser diffraction method. The analyses were carried out using a Mastersizer 2000 by Malvern Panalytical.

X-ray powder diffraction (XRD) was performed using an Olympus BTX 470 II diffractometer.

Thermogravimetric analyses were carried out by using a TGA Q500, TA Instruments. Samples of 10–15 mg were placed in Al_2O_3 crucibles, and the runs carried out in high purity N_2. The heating rate was 20 °C/min over the 50–1000 °C interval.

All flame tests and LOI measurements were carried out by using a SA ASSOCIATES Oxygen Index apparatus on specimens with dimension of 10 × 6 × 3 mm and according to ASTM D2863. A burner flame was applied on the top of a vertically oriented bar placed in a test column where a mixture of oxygen and nitrogen flows. LOI value represents

the minimum concentration of oxygen (%) in the gas mixture necessary to support the combustion of the material. The initial concentration of oxygen is chosen arbitrarily.

3. Results

3.1. Study of the Amount of Coupling Agent

Formulations frequently used in the cable industry were selected and investigated (Table 4), i.e., by varying the nature of the polymer matrix (a blend of EVA 28 with a secondary polymer and ethylene α-olefin copolymer) and the mineral filler, respectively. Moreover, among the formulation ingredients, ULDPE-g-MAH represents the most effective coupling agent for the preparation of highly compatible polymeric composites [25].

Table 4. Basic formulation of the composites.

Ingredients	wt.%	Role
EVA 28–3	27	Vinyl acetate comonomer contributes to flexibility, polarity, good behavior in fire tests (char forming)
Ethylene α-olefin copolymer	7–12	Resistance to deformation at high temperature
Mineral filler	56–64	Flame retardant
ULDPE–g–MAH	0–5	Coupling agent
Silicon MB	1	Processing aid

Notably, ULDPE-g-MAH is an ultra-low density polyethylene (ULDPE) with grafted maleic anhydride (MAH), which has the function of reducing the interphase tension with the n-MDH fillers [26]. Indeed, the presence of the grafted MAH units generates effective coupling interactions with the hydroxyl groups of the filler surface during the mixing process, thus enhancing its phase dispersion within the polymer matrix and, in turn, the mechanical properties of the final composite [4].

Silicon MB is a further ingredient used as processing aid in order to facilitate the processability of compounds that contain large amounts of mineral fillers that cause an excessive viscosity [27]. The silicon MB is effective at 0.1–2 wt.% and is incompatible with the polymeric matrix, thus causing the so-called "slipping" action (also called *external lubricants*). Actually, the silicon MB during the melt-processing is ejected from the polymer matrix, thus promoting friction decreasing during blending by the metal walls of the mixer and the occurrence of a smoother surface of the extrudate [28].

The first set of experiments was designed by varying the amount of ULDPE-g-MAH, used as coupling agent. Generally, an amount equal to 3–5 wt.% was added to the formulations to guarantee the mechanical properties of the final compound. Six different formulations were made as reported in Table 5.

**Table 5.** Formulations vs. dosage of maleated coupling %.

Ingredient	Trade Name	A (%)	B (%)	C (%)	D (%)	E (%)	F (%)
EVA 28–3	Elvax 265	27	27	27	27	27	27
C8–ULDPE	Engage 8450	12	11	10	9	8	7
ULDPE–g–MAH	Fusabond N 525	0	1	2	3	4	5
N–MDH	Ecopiren 3.5	60	60	60	60	60	60
Silicon MB	Silmaprocess AL1142A	1	1	1	1	1	1

The mechanical properties have been summarized in Table 6 and compared as a function of the dosage of the coupling agent in Figure 1.

Table 6. Mechanical properties of the composites vs. dosage of the maleated coupling agent (ULDPE-g-MAH, wt.%).

Properties	Unit	A 0%	B 1%	C 2%	D 3%	E 4%	F 5%
Density [1] (±0.1)	g/cm^3	1.475	1.471	1.474	1.469	1.471	1.471
Calculated Density	g/cm^3	1.472	1.471	1.471	1.470	1.469	1.469
MFI [2]	g/10 min	14.7 ± 0.7	11.6 ± 0.6	10.3 ± 0.5	9.2 ± 0.5	7 ± 0.3	6.6 ± 0.4
Young's Modulus	MPa	99 ± 6	94 ± 12	89 ± 8	81 ± 7	74 ± 12	70 ± 2
Tensile Strength [3]	MPa	7.0 ± 0.8	9.3 ± 0.9	9.9 ± 0.8	11.6 ± 0.7	11.8 ± 0.5	12.9 ± 0.7
Elongation at break [3]	%	127 ± 45	140 ± 30	168 ± 24	173 ± 20	199 ± 18	187 ± 11

[1] ASTM D792, [2] 21.6 kg @ 190 °C, [3] ISO 37 Type-2.
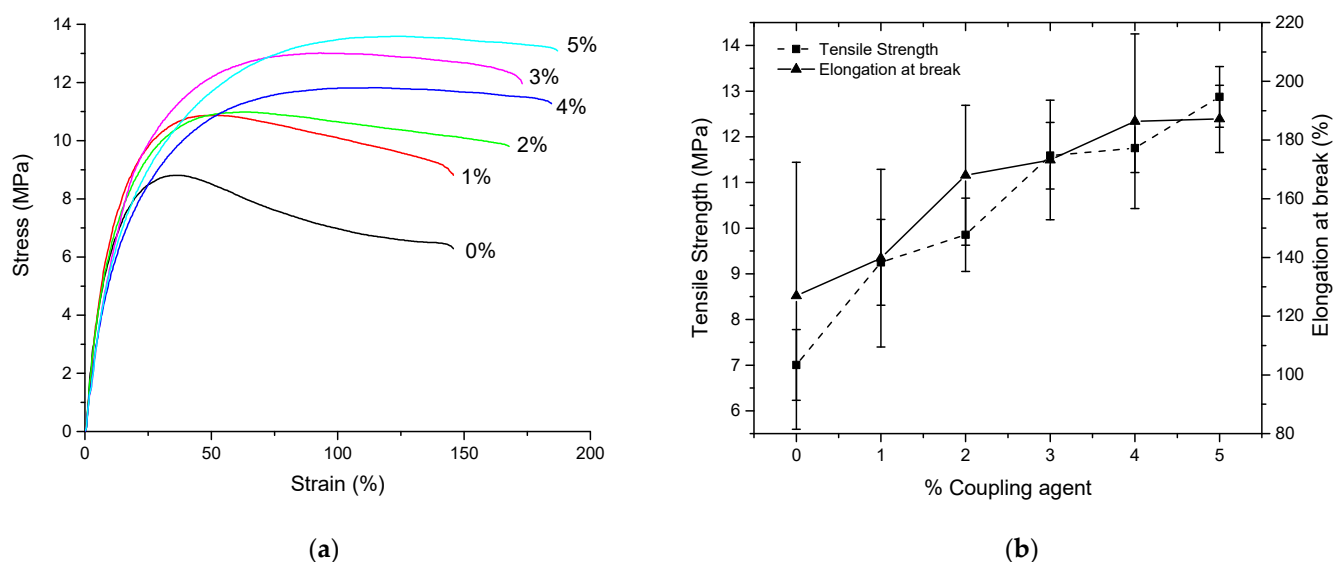
Figure 1. Stress–strain curves (**a**) of the prepared composites and plot of the tensile strength and elongation at break (**b**) as a function of the maleated coupling agent (ULDPE-g-MAH, wt.%).

Notably, tensile strength and elongation at break are both enhanced by increasing the dosage of the coupling agent thanks to the double effect provided by the compatibilizing grafted MAH groups and the flexibility conferred by the ULDPE matrix [29]. Moreover, MFI decreases as expected by increasing the coupling agent content as consequence of the enhanced interaction between the polymeric matrix and the fillers particles (Table 6). Based on the obtained results, the optimal amount of the ULDPE-g-MAH coupling agent utilized for the further experiments was the 3 wt.%, since it confers to the composite the best trade-off between mechanical (11.6 ± 0.7 MPa of tensile strength and 173 ± 20 % of elongation at break) and rheological properties (9.2 g/10 min).

3.2. Variation of Content of n-MDH

Table 7 and Figure 2 report the results of tests obtained on composites produced using the 3 wt.% of coupling agent and varying the n-MDH dosage in the range between 56 wt.% (33.8 vol.%) and 64 wt.% (41.6 vol.%), aimed to find the required amount of filler for providing the best trade-off between good flame retardant properties (expressed by Limited Oxygen Index LOI, usually >32 %O_2 [30,31]) and adequate mechanical properties required for cable application (i.e., tensile strength > 10 MPa and elongation at break >150% [23]).

Table 7. Mechanical and flame retardant properties of the composites vs. content of n-MDH (wt.%).

Properties	Unit	56%	58%	60%	62%	64%
Density (± 0.1)	g/cm^3	1.416	1.445	1.469	1.502	1.529
Calculated Density	g/cm^3	1.418	1.444	1.470	1.497	1.526
MFI	g/10 min	12.4 ± 0.6	11.4 ± 0.6	9.2 ± 0.5	5.6 ± 0.3	3.8 ± 0.2
Young's Modulus	MPa	70 ± 5	80 ± 7	81 ± 7	83 ± 6	97 ± 7
LOI (± 0.5) *	%	34	34	36	37	40
Tensile Strength	MPa	10.9 ± 0.8	10.9 ± 0.7	11.6 ± 0.7	11.2 ± 0.8	12.4 ± 0.8
Elongation at break	%	243 ± 29	252 ± 28	173 ± 20	151 ± 9	119 ± 14

Formulation is: 23 to 31 wt.% EVA28, 9 wt.% Engage 8450, 3 wt.% ULDPE-g-MAH, 56 to 64 wt.% n-MDH, 1 wt.% Silicon MB., * ASTM D2863.

(**a**)   (**b**)
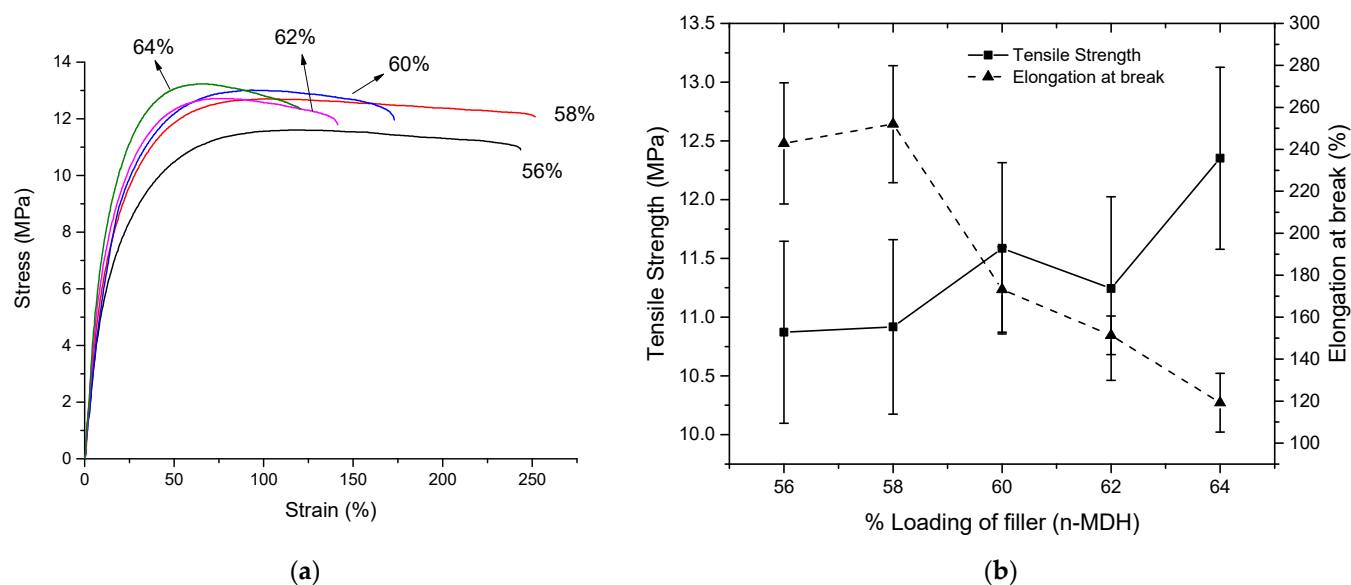
Figure 2. Stress–strain curves (**a**) of the prepared composites and plot of the tensile strength and elongation at break (**b**) as a function of the n-MDH content.

Notably, a narrow range of 56–64 wt.% of mineral filler was used being frequently used to prepare halogen-free flame retarding polymer composites [32].

Values reported in Table 4 and Figure 2 evidence the role of the filler loading in increasing the rigidity of the final composites (i.e., Young's modulus becomes higher) and tensile strength from 10.9 ± 0.8 MPa to 12.4 ± 0.8 MPa, and adversely affecting the elongation at break that decreased from $243 \pm 29\%$ to $119 \pm 14\%$. Based on the results obtained, we selected the 60 wt.% of n-MDH as the best trade-off between elongation at break ($173 \pm 20\%$) and tensile strength (11.6 ± 0.7 MPa) to be adopted for all subsequent formulations. This selection was also supported by the LOI value of 36% that indicates that the compound is not flammable, and by the MFI around 10 g/10 min, that evidence a good blend processability.

3.3. Variation of Type of Polyolefin Used in Combination with EVA28

Since the plastic sheath used in electrical cables must be resistant to deformation at high temperatures as well, a secondary polymeric component is introduced in the formulations. EVA 28, with a melting temperature around 70 °C is not rigid enough above this temperature, and polymers like PE or PP are generally added to confer the cable resistance at higher temperatures [33–35]. Among the listed polymers, those based on

VLDPE and mLLDPE (low density polyethylene copolymers based on octene, hexene, or butene obtained through metallocene catalysts) are preferred, being helpful for the elongation at break and primarily on the workability during processing. ULDPE (ethylene α-olefin copolymer) and C_3-C_2 copolymers, produced with both metallocenic and Ziegler–Natta catalyst, result the most preferred since the more amorphous character and long chain branching better withstand high percentages of fillers [23–36].

Therefore, different composites made by EVA28/polyolefin blends in a 3:1 weight ratio and containing the 3 wt.% of ULDPE-g-MAH, 60 wt.% of n-MDH and 1% of Silicon MB were studied and the results reported in Table 8 and Figure 3.

Table 8. Mechanical properties of EVA28/polyolefin blend with different type of poly (ethylene-co-α-olefin).

Properties	Unit	4 C_4-LLDPE	5 C_6-mLLDPE	6 C_6-mLLDPE	7 C_6-mLLDPE	8 C_6-mLLDPE	9 C_8-ULDPE	10 C_4-VLDPE
Second polymer	Trade Name	Flexirene CL10U	Exceed 3518	Exceed 3812	Evolue SP1071	Exceed 0015XC	Engage 8450	Clearflex MBQ0
Density (±0.1)	g/cm^3	1.473	1.478	1.477	1.475	1.473	1.469	1.478
Calculated Density	g/cm^3	1.474	1.474	1.472	1.472	1.474	1.470	1.472
MFI	g/10 min	10 ± 0.5	5.7 ± 0.3	7.1 ± 0.4	10.3 ± 0.5	14.9±0.7	9.2 ± 0.5	13 ± 0.7
Young's Modulus	MPa	88 ± 5	105 ± 5	95 ± 9	96 ± 4	95 ± 6	81 ± 7	101 ± 10
Tensile Strengh	MPa	14.1 ± 1.3	12.7 ± 0.5	11.9 ± 0.8	12.5 ± 0.8	12.0 ± 0.7	11.6 ± 0.7	11.3 ± 0.7
Elongation at Break	%	114 ± 11	149 ± 16	138 ± 17	126 ± 20	111 ± 12	173 ± 20	194 ± 18

Formulation is: 27 wt.% EVA28, 9 wt.% poly (ethylene-co-α-olefin), 3 wt.% ULDPE-g-MAH, 60 wt.% n-MDH, 1 wt.% Silicone MB.
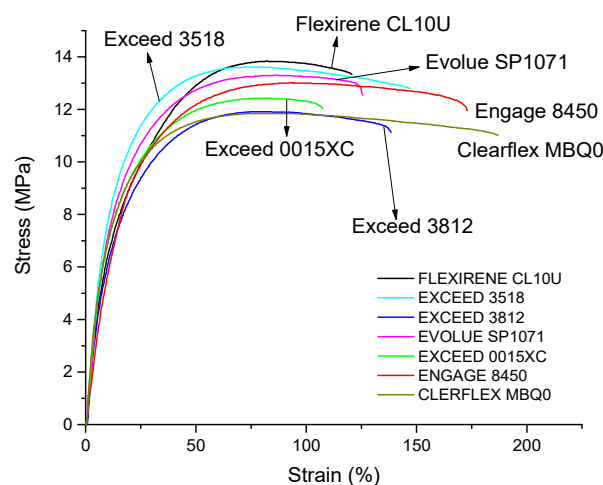

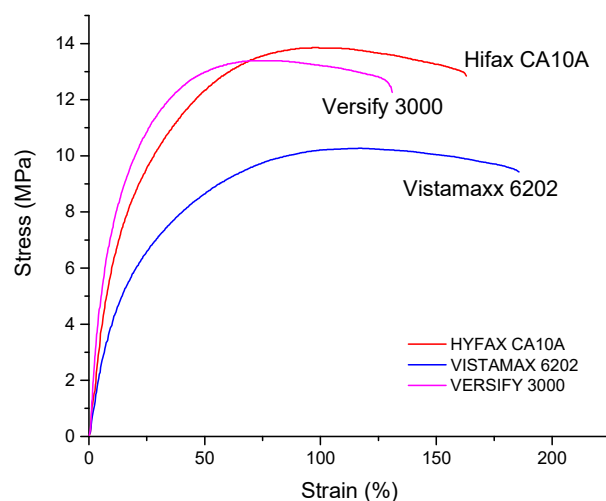**Figure 3.** Stress–strain curves of the composites as a function of the different type of poly (ethylene-co-α-olefin).

The composite with the best mechanical properties in terms of elongation at break (173 ± 20%), tensile strength (11.6 ± 0.7 MPa) and Melt Flow Index (9.2 ± 0.5 g/10 min) is the number 9, that is based on ULDPE characterized by the lowest density and crystalline content of 29%. For this reason, this secondary Engage 8450 polymer was selected as the reference polymer for the subsequent formulations.

As previously mentioned, among the secondary polymers studied heterophasic copolymers based on PP/EP rubber were investigated in this work as well, and the results gathered from the mechanical tests are reported in Table 9 and Figure 4.

Table 9. Mechanical properties of the EVA28/polyolefin blends with different type of C_3-C_2 copolymers.

Properties	Unit	11 Heterophasic PP-EPR	12 C_3-C_2 Copolymer	13 C_3-C_2 Copolymer
Second polymer	Trade Name	Hifax CA10A	Vistamaxx 6202	Versify 3000
Density (± 0.1)	g/cm^3	1.472	1.472	1.472
Calculated Density	g/cm^3	1.470	1.470	1.470
MFI	g/10 min	5.6 ± 0.3	11 ± 0.6	13 ± 0.6
Young's Modulus	MPa	76 ± 3	58 ± 8	109 ± 7
Tensile Strength	MPa	12.7 ± 0.5	10.9 ± 0.7	11.9 ± 0.9
Elongation at Break	%	163 ± 12	181 ± 20	128 ± 24

Formulation is: 27 wt.% EVA28, 9 wt.% C_3-C_2 copolymer, 3 wt.% ULDPE-g-MAH, 60 wt.% n-MDH, 1 wt.% Silicon MB.

Figure 4. Stress–strain curves of the composites as a function of the different type of C3-C2 copolymers.

Stress–strain curves show composite performances in line with those obtained by using a polyethylene-based secondary polymer. Therefore, considering the higher costs and similar mechanical properties provided, heterophasic copolymers are no longer investigated in this work. Nevertheless, considering the aesthetic advantages conferred to the composite surface, future works will be addressed also on considering this feature.

3.4. Variation of Type of Mineral Filler Used in Combination with Natural n-MDH

As mentioned earlier, among all the mineral fillers used in electrical cable market, magnesium hydroxide (MDH) shows the required performances in polyolefins with competitive cost thanks to its natural origin and high earth abundance. In order to investigate the effect provided by the nature of the MDH filler, n-MDH was replaced with the synthetic one (s-MDH).

The XRD diffractogram in Figure 5 shows more intense reflections of s-MDH (blue curve) that are associated to a more crystalline character with respect to n-MDH (red curve), i.e., 94% vs. 89%, respectively. The lower crystallinity content of n-MDH is attributed to the presence of $CaCO_3$, $MgCO_3$ and silicates impurities in the composition of the filler as a result of the milling processes of brucite as mentioned earlier [18].
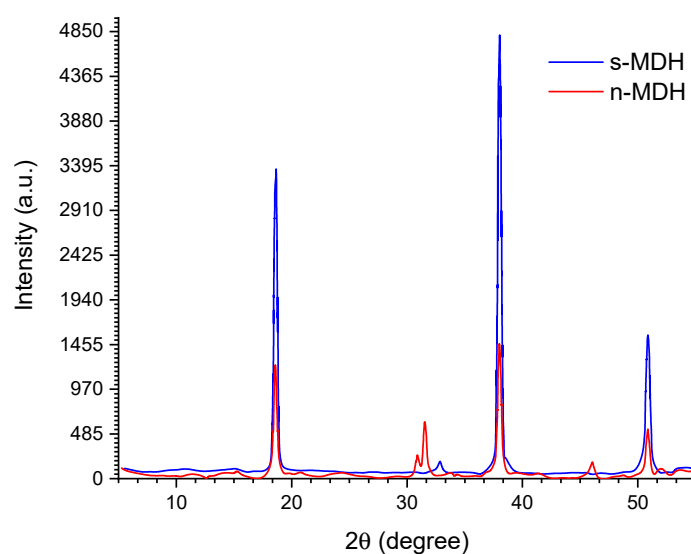
Figure 5. XRD analysis of n-MDH (red) and s-MDH (blue).

Nevertheless, the lower crystallinity of n-MDH is not a relevant issue for the final properties of the composite, since its mechanical characteristics are mainly governed by the shape of the filler particles [37]. Notably, SEM micrographs (Figure 6) show n-MDH particles with an irregular needle-like shape with respect to the more regular hexagonal crystal geometry displayed by s-MDH that possibly promotes effective adhesion with the polymer. This is reflected on the mechanical properties of the derived composites (Table 10 and Figure 7) that showed remarkable higher elongation at break when s-MDH is used, i.e., $272 \pm 71\%$ against $173 \pm 20\%$ for n-MDH.
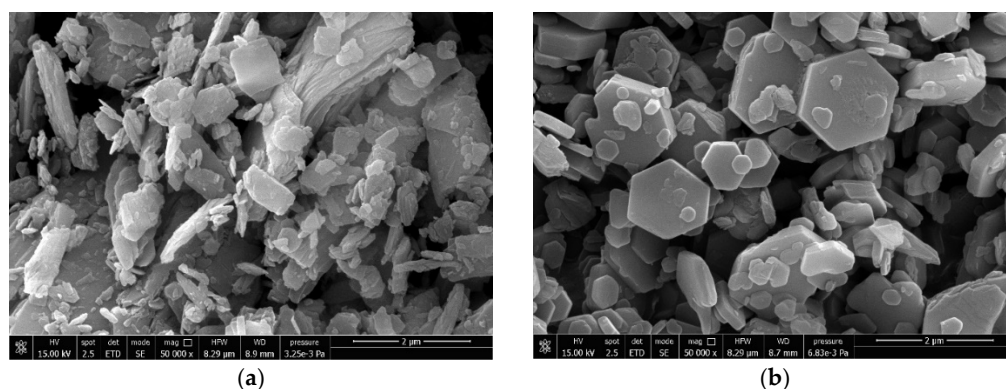

| (a) | (b) |

Figure 6. SEM micrographs of n-MDH (**a**) and s-MDH (**b**) (scale bar 2 μm).

Table 10. Mechanical properties of the composites containing the n-MDH or s-MDH filler.

Properties	Unit	9 Ecopiren 3.5 (n-MDH)	14 Magnifin H5 (s-MDH)
Density (± 0.1)	g/cm^3	1.469	1.462
MFI	g/10 min	9.2 ± 0.5	12.8 ± 0.6
Young's Modulus	MPa	81 ± 7	72 ± 19
Tensile Strength	MPa	11.6 ± 0.7	11.8 ± 0.2
Elongation at break	%	173 ± 20	272 ± 71

Formulation is: 27 wt.% EVA28, 9 wt.% Engage 8450, 3 wt.% ULDPE-g-MAH, 60 wt.% n-MDH or s-MDH, 1 wt.% Silicon MB.
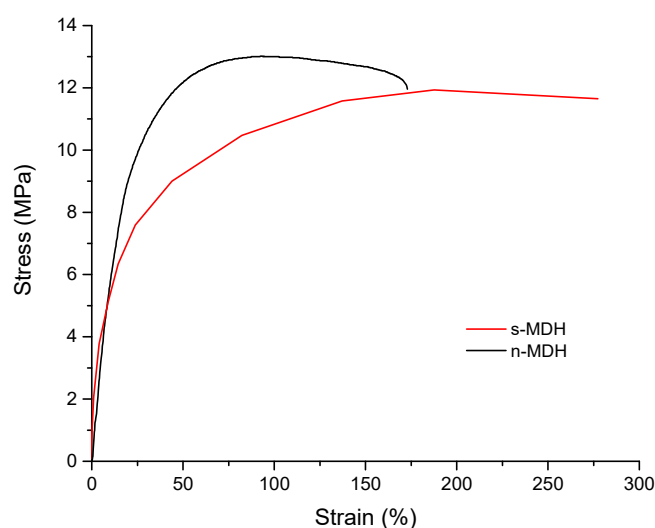
Figure 7. Stress–strain curves for the composites as a function of the different type of filler: n-MDH (black curve) or s-MDH (red curve).

Nevertheless, aimed at cost optimization for the production of the final composites, n-MDH is still preferred as the primary flame retardant instead of the more performant but more expensive s-MDH.

Among the investigated fillers, Kisuma 5A is a synthetic magnesium hydroxide coated with stearic acid. It was found that the application of an organic agent on the particles did not change the size distribution, but it caused a significant decrease of the specific surface area up to 4–7 m^2/g (see experimental part) without the formation of particles aggregates. The reduction of the surface area was possibly addressed to the occlusion of pores on the brucite surface and possibly favoured higher elongation at break and lower values of tensile strength [38].

The SEM micrographs reported in Figure 8 show that among the natural fillers investigated huntite that is a mix of magnesium and calcium carbonate (Figure 8e) shows particles with an irregular lamellar like shape, in contrast with the uniform and rounded particles of calcium carbonate coated with stearic acid (Figure 8a). As expected, the particles made by synthetic fillers show regular shape and uniform size. Notably, coated magnesium hydroxide (Figure 8c) shows more rounded particles while calcium carbonate (Figure 8d) and boehmite (Figure 8b) particles are almost similar to spheres.
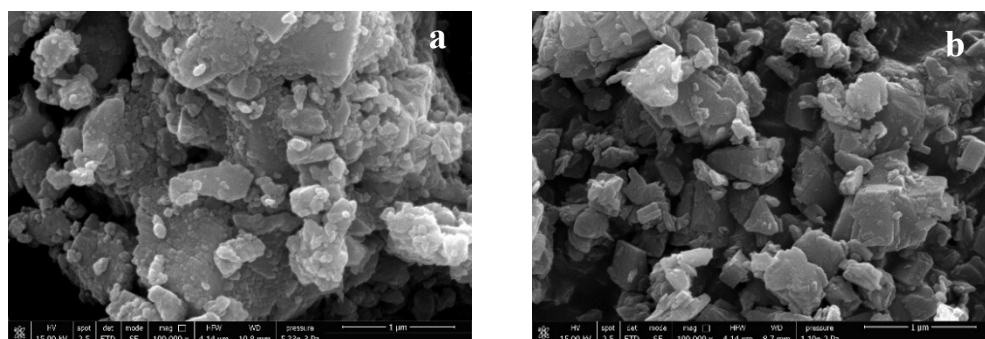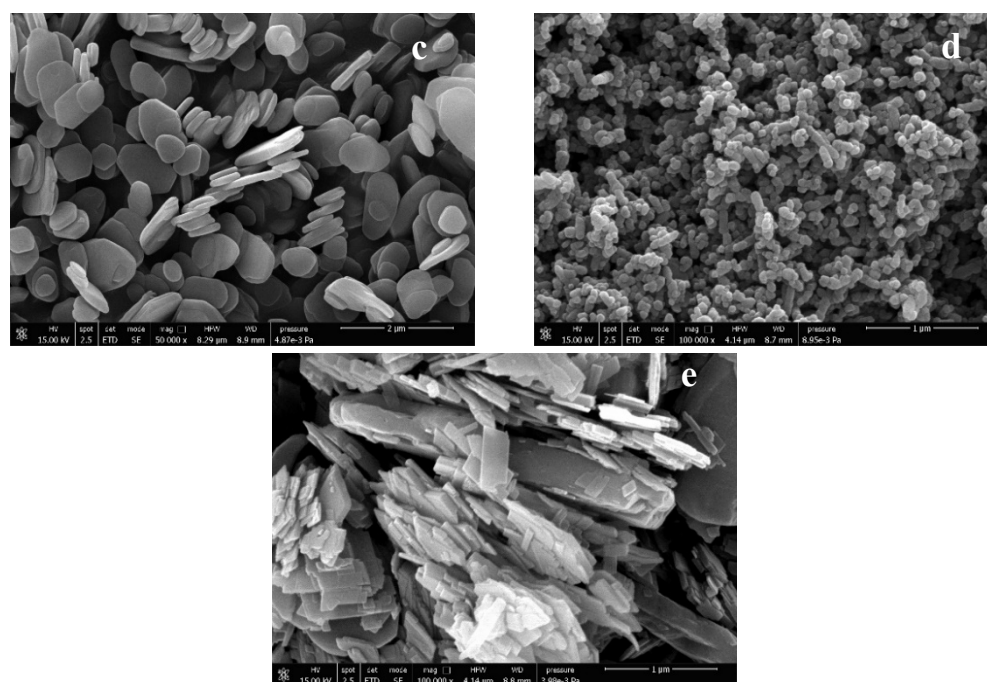

Figure 8. *Cont.*

Figure 8. SEM micrographs of the analyzed fillers: $CaCO_3$ stearic coated (**a**), scale bar 1 µm), bohmite (**b**), scale bar 1 µm), synthetic MDH stearic coated (**c**), scale bar 2 µm), synthetic $CaCO_3$ (**d**), scale bar 1 µm) and huntite (**e**), scale bar 1 µm).

In order to identify possible synergies between mineral fillers in terms of rheology and mechanical properties of the final composites, n-MDH was selected as the main flame retardant in combination with the 15 wt.% of a secondary filler of natural or synthetic origin. The 3:1 weight ratio was determined considering the optimized trade-off between possible advantages and costs (Tables 11 and 12).

Table 11. Mechanical properties of the composites containing a mix of n-MDH with a natural filler.

| Properties	Unit	9 n-MDH	15 Coated CaCO₃	16 Huntite/Hydromagnesite
Secondary filler	Trade Name	Ecopiren 3.5	Polyplex 0	Portafill H5
Density (±0.1)	g/cm³	1.469	1.487	1.489
MFI	g/10 min	9.2 ± 0.5	10.4 ± 0.5	6.6 ± 0.3
Young's Modulus	MPa	81 ± 7	65 ± 4	87 ± 4
Tensile Strength	MPa	11.6 ± 0.7	10.1 ± 0.5	11.8 ± 0.2
Elongation at break	%	173 ± 20	198 ± 16	177 ± 24

Formulation is: 27 wt.% EVA28, 9 wt.% Engage 8450, 3 wt.% ULDPE-g-MAH, 60 wt.% n-MDH (number 9) or n-MDH in combination with a secondary natural filler (3:1 ratio), 1 wt.% Silicon MB.

Table 12. Mechanical properties of the composites containing a mix of n-MDH with a synthetic filler.

Properties	Unit	9 n-MDH	17 AlOOH	18 s-MDH	19 Coated s-MDH	20 Coated s-MDH	21 Coated CaCO$_3$
Secondary filler	Trade Name	Ecopiren 3.5	Aluprem TB 1/T	Magnifin H5	Magnifin H5 GV	Kisuma 5A	Winnofil S
Density (±0.1)	g/cm^3	1.469	1.501	1.479	1.466	1.471	1.482
MFI	g/10 min	9.2 ± 0.5	8.8 ± 0.4	8.8 ± 0.4	10.3 ± 0.5	9.6 ± 0.5	4.2 ± 0.2
Young's Modulus	MPa	81 ± 7	72 ± 6	72 ± 4	76 ± 6	71 ± 3	74 ± 9
Tensile Strength	MPa	11.6 ± 0.7	11.3 ± 0.6	13.4 ± 0.4	12.6 ± 0.5	13.1 ± 0.3	11.8 ± 0.1
Elongation at break	%	173 ± 20	201 ± 17	188 ± 14	190 ± 15	179 ± 22	234 ± 30

Formulation is: 27 wt.% EVA28, 9 wt.% Engage 8450, 3 wt.% ULDPE-g-MAH, 60 wt.% n-MDH (number 9) or n-MDH in combination with a secondary synthetic filler (3:1 ratio), 1 wt.% Silicon MB.

Partial replacement of n-MDH with natural fillers gives rise in the case of Polyplex 0 (stearic coated CaCO$_3$) to a slight improvement of the elongation at break (198 ± 16%) but with a lower value of tensile strength (10.1 ± 0.5 MPa) (Figure 9). This behavior could be addressed to the CaCO$_3$ surface coated by stearic acid. The coating is used to reduce the high surface energy of CaCO$_3$ particles and their effective interactions, thus limiting the probability of generating cohesive agglomerates. The coated organic film represents the interface between the filler and the polymer matrix, and hence influences the wetting and adhesion properties of the two involved phases [39].
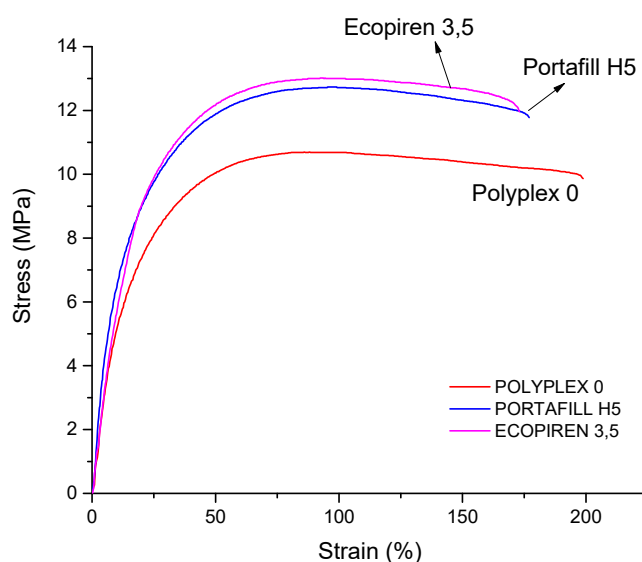
Figure 9. Stress–strain curves of the composites containing a mix of n-MDH with a natural filler.

As reported by Rothon [4], the stearic chain lengths used for filler coating are too short to entangle with a polymer matrix, thus usually promoting a decrease in its ultimate strength, although significant improvements in elongation and toughness are evidenced. In thermoplastics it is generally reported that fatty acid treatments reduce melt viscosity, improve filler dispersion, decrease modulus, reduce tensile strength, but improve elongation and impact resistance, as also confirmed by the results obtained in sample 15 (red curve).

On the contrary, in the case of Portafill H5 (huntite), the curves are practically superimposed (blue and pink curves), possibly because both huntite and n-MDH particles are

characterized by the same irregular structure, therefore interacting in the same way with the polymer matrix (Figure 8e).

A partial replacement of n-MDH with synthetic minerals gives rise to an improvement in the tensile strength and the elongation at break, particularly evidenced in the case of samples 17 and 21 based on secondary fillers such as boehmite (AlOOH, Aluprem TB 1/T) and synthetic $CaCO_3$ coated with fatty acids (Winnofil S), respectively (Figure 10). As mentioned earlier, the better dispersion flanked by poor adhesion with the polymer matrix caused by filler coating is again reflected on sample 17 that is characterized by a higher value of elongation at break (234 ± 30%) in contrast with the use of n-MDH (173 ± 20%). In particular, improved elongation at break when using boehmite (201 ± 17%) may be due to the formation of agglomerates that weakly interact with polymer matrix, thus providing a lower value of tensile strength (11.3 ± 0.6 MPa). However further studies are needed to better understand the filler-polymer interactions established because they depend on many factors such as particle size, surface treatment, polymer matrix polarity and others. Nevertheless, the differences in mechanical properties among EVA samples filled with different flame retardant fillers widely satisfy the standard requirements for cable applications and a primarily study is already complete to optimize a recipe for cable application.
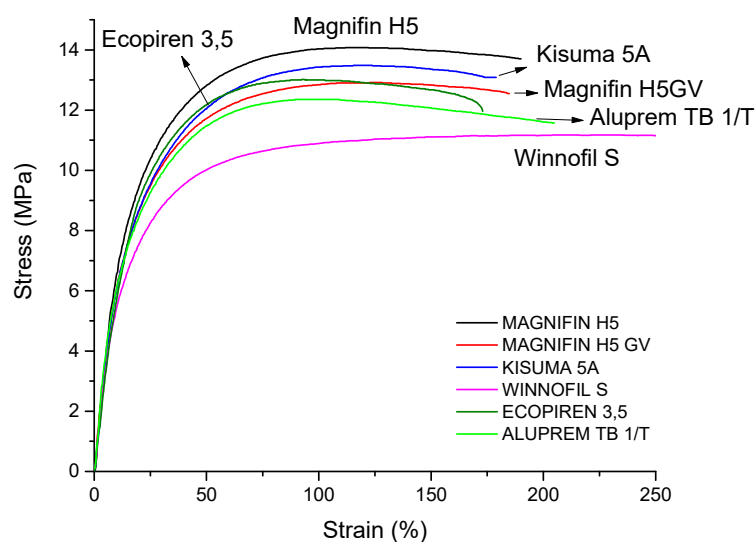

Figure 10. Stress–strain curves of the composites containing a mix of n-MDH with a synthetic filler.

3.5. Flame Retardant Properties

We eventually investigated the flame retardant properties of the most promising composites in terms of the Limiting Oxygen Index (LOI). Among them, those made by a mixture of n-MDH with boehmite (AlOOH, Aluprem TB 1/T, number 17), n-MDH with s-MDH (number 18), and n-MDH with synthetic $CaCO_3$ coated with fatty acids (Winnofil S, number 21) were investigated. Formulations only containing n-MDH and s-MDH as mineral filler were also tested as a reference (Table 13).

In this case, LOI was found as 36% for the composite containing n-MDH (36%) and 38.5% for that made by s-MDH. This difference was possibly addressed to the better dispersion of the synthetic particles in polymer matrix as discussed earlier combined by the presence in n-MDH of calcium and magnesium carbonate (see TGA curves in Figure S1). This contamination worsened the flame retardant features of the composites due to their higher decomposition temperature [40]. In fact, the lowest LOI value of 33% was determined for the formulation number 21 based on a mixture of n-MDH and $CaCO_3$.

Table 13. Flame retardant properties of the composites containing n-MDH, s-MDH and a mixture of n-MDH with a synthetic filler.

Properties	Unit	9 n-MDH	14 s-MDH	17 AlOOH	18 s-MDH	21 Coated CaCO$_3$
Secondary filler	Trade Name	100% Ecopiren 3.5	100% Magnifin H5	15% Aluprem TB 1/T	15% Magnifin H5	15% Winnofil S
LOI	%	36	38,5	37	36.5	33

Formulation is: 27 wt.% EVA28, 9 wt.% Engage 8450, 3 wt.% ULDPE-g-MAH, 60 wt.% n-MDH (number 9) or s-MDH (number 14) or n-MDH in combination with a secondary synthetic filler (3:1 ratio), 1 wt.% Silicon MB.

Among the other formulations, it is possible to notice an improvement of LOI when n-MDH is used in combination with s-MDH (36.5%) and boehmite (37%), though not strikingly relevant. However, this result is in agreement with previous works conducted in our laboratory [41] and it could be possibly addressed to its smaller particle size (D_{50} = 1.21 µm) [42].

4. Discussion

Outer sheathing compounds of electrical cable require robust mechanical properties, good surface quality, and flaming resistance. These performance attributes are achieved by the incorporation of mineral fillers into a polyolefin polymeric matrix. Several secondary polymers in combination with EVA and metal hydroxides and carbonates were evaluated for their effects on tensile properties, LOI and rheology.

Many formulations were studied to determine the optimal dosage of the utilized ingredients and to maximize the ultimate mechanical properties. Our studies showed that the presence of a coupling agent (ultra-low density polyethylene with grafted maleic anhydride, ULDPE-g-MAH) is necessary to obtain good tensile strength and elongation at break. This is due to the establishment of interactions between the hydrophobic and apolar polymer matrix and the hydrophilic and polar filler particles promoted by the presence of the coupling agent, that is a ULDPE grafted with succinic anhydride groups. In particular our investigations determined that the optimal dosage of this ingredient was equal to 3% by weight, as in addition to obtaining good values of tensile strength and elongation at break, it also provided rather high MFI values (Melt Flow Index, corresponding to low melt viscosity), indicating a better processability of the compound once melted.

Further tests were conducted to assess the optimal dosage of filler to provide good mechanical properties but also low flammability. From the results obtained, the best compromise was the use of the 60% by weight of filler: it gave good mechanical properties, good processability and a relatively high value of LOI.

Therefore, the basic formulations consisted of 60% by weight of mineral filler, 3% by weight of coupling agent, 1% by weight of processing aid (silicon MB) and the remaining 36% to the polymer matrix consisting of EVA28 and a secondary polymer in 27 % and 9% by weight, respectively.

It was found that different magnesium hydroxides impart different mechanical properties: n-MDH provided worst mechanical properties in comparison with the synthetic s-MDH, but at very high costs. Therefore, different formulations were studied by varying the type of polymer matrix and using a mixture of n-MDH combined with other kind of fillers (in a 3:1 ratio using as main filler n-MDH) aiming to enhance composite properties. On this account, we found that the best synergistic effect is achieved using a filler blend system containing n-MDH as main filler in combination with boehmite.

5. Conclusions

In this work, several secondary polymers in combination with EVA28 and metal hydroxides and carbonates were tested to investigate their influence on the tensile properties

and LOI of the final composites. Our studies showed that the presence of the 3 wt.% of a coupling agent (ultra-low density polyethylene grafted with maleic anhydride, ULDPE-g-MAH) is necessary to obtain good tensile strength and elongation at break, and the 60 wt.% of filler to endow composites with good mechanical properties, processability, and a relatively high value of LOI of 36%. The use of n-MDH as filler was demonstrated to partly comply with the mechanical properties required in cables parameters, i.e., displaying acceptable elongation at break of about 170%. Higher mechanical performances were gathered by using s-MDH that is characterized by higher crystallinity and regular particles' hexagonal geometry, but its cost suggested the use of more convenient synergic combinations between n-MDH and natural and synthetic fillers. More specifically, the best results were obtained by using boehmite and synthetic $CaCO_3$ coated with fatty acids, whose shape and surface treatment are associated with a reduction in filler matrix adhesion and an increase in the dispersion quality of the filler thus giving interesting elongation at break of about 206 and 230%. Moreover, in the case of boehmite, the best flame retardant properties with a LOI of 37% was eventually determined.

Overall, the present research provided a complete and optimized recipe for the formulation of polymer composites characterized by the required flame retardant and mechanical features in electric cables applications.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/micro1010008/s1, Figure S1: TGA n-MDH (blue) vs. s-MDH (red).

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