



Article

Effect of Carbonate Mineral Fillers on the Dielectric Properties and Fire Resistance of Polar and Non-Polar Halogen-Free Flame-Retardant Polymer Compounds

Konstantinos G. Gatos ¹, Nikolaos Apostolopoulos ^{1,†}, Anastasios C. Patsidis ² and Georgios C. Psarras ^{2,*}

¹ Terna Mag S.A., 11526 Athens, Greece; kgatos@ternamag.com (K.G.G.);
nik.apostolopoulos@ppcgroup.com (N.A.)

² Smart Materials & Nanodielectrics Laboratory, Department of Materials Science, School of Natural Sciences,
University of Patras, 26504 Patras, Greece; patsidis@upatras.gr

* Correspondence: G.C.Psarras@upatras.gr; Tel.: +30-2610996316

† Current address: PPC S.A., 34500 Aliveri, Greece.

Abstract: In the present work, carbonate minerals are added in non-polar and polar polymer matrices to develop halogen-free flame-retardant composites. The examined fillers of calcium carbonate and magnesium carbonate delivered improved rheological performance in both non-polar (PE) and polar (EVA/PE) polymer compounds compared to the natural magnesium hydroxide and huntite/hydromagnesite mineral fillers. The presence of EVA in the matrix enhanced the mechanical behavior of all compounds in tensile testing. The thermal stability of the composites was particularly improved for the polar systems with the incorporation of the carbonate minerals, as this was evidenced under thermogravimetric analysis. The dielectric behavior of the fabricated systems was examined via broadband dielectric spectroscopy. The HFFR compounds attained higher values of the real part of dielectric permittivity from the unreinforced systems in the whole frequency and temperature range of the conducted tests. This behavior is ascribed to the higher permittivity values of the fillers with respect to the polymer matrices and the occurrence of interfacial polarization. All minerals improved the flame retardancy of the compounds in terms of LOI values, while the addition of EVA yielded further improvements, especially for the magnesium carbonate and the magnesium hydroxide minerals.

Keywords: polymer composites; flame retardancy; thermal stability; dielectric properties; HFFR



Citation: Gatos, K.G.; Apostolopoulos, N.; Patsidis, A.C.; Psarras, G.C. Effect of Carbonate Mineral Fillers on the Dielectric Properties and Fire Resistance of Polar and Non-Polar Halogen-Free Flame-Retardant Polymer Compounds. *J. Compos. Sci.* **2024**, *8*, 529. <https://doi.org/10.3390/jcs8120529>

Academic Editor: Francesco Tornabene

Received: 22 October 2024

Revised: 2 December 2024

Accepted: 4 December 2024

Published: 14 December 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Polymer matrix composites are utilized as engineering materials in many sectors, including automotive, marine, aviation, and aerospace industries, as well as in civil construction, packaging, and leisure products. Polymer composites exhibit many advantages, such as easy fabrication and shaping, low weight, thermomechanical stability, environmental and corrosion resistance, and thermal and electrical insulation, at a relatively low cost. Because polymers mainly consist of hydrocarbon macromolecules that are burnt easily, safety issues in various applications are raised. The flame retardancy (FR) of polymer matrix composites is enhanced by employing suitable inclusions and/or by developing FR coatings [1–3].

Mineral fillers are currently regarded as cost-effective additives for various halogen-free flame retardant (HFFR) applications. These inorganic flame retardants relate, among others, to metal oxides and hydroxides, phosphorus, silicon, or boron compounds. Their behavior is characterized by enhanced thermal stability, non-volatility, and long-lasting performance. When decomposed metal hydroxides release water, this has a beneficial effect by reducing both the temperature of the polymer matrix and the concentration of

oxygen in the ambient air [3,4]. The most common category of metal hydrates is well-accepted to present no risk to human health or the environment; thus, they are considered environmentally friendly flame-retardant fillers [5]. Nevertheless, their incorporation into the polymeric matrix requires a significant amount of filler fraction for imparting adequate flammability resistance. Therefore, the respective composite usually suffers from mechanical property deterioration, as well as difficulties in compounding [6]. This latter is especially apparent in cases where the extrusion of thin filaments is required, such as in 3D printing applications [7,8].

Polyethylene is a thermoplastic polymer with numerous applications, wherein its flame retardancy becomes a prerequisite in some cases, such as wire and cable [9], electric enclosures, building panels, etc. It is often blended with compatibilizers in complex recipes to get the most out of the compound [10,11].

Several mineral fillers of different origins have been investigated for their applicability in polyethylene compounds [12]. Nowadays, widely accepted mineral fillers for polyethylene (PE) and poly(ethylene co-vinyl acetate) (EVA) relate to hydroxide minerals, such as aluminum tri-hydroxide [13] and magnesium di-hydroxide [14]. Their flame-retardant action stems mainly from a combination of parameters, such as the reduction of the overall combustible content in the respective polymer composites, the energy absorption required for their thermal decomposition, the release of water during mineral decomposition, which dilutes the combustible gases, as well as the remaining surface mineral oxide thermal insulating layer [15]. A fire scenario begins with the ignition event, wherein a source of heat meets the polymeric material, the fuel. Combustion progresses depending upon the rate of fire growth, where the flammable degradation species react with the oxygen in the air to produce more flames and heat. In the fully developed fire, a continuous heat flux is transferred back to the fuel, maintaining the flow of volatile products [16]. The flame retardants function in the flame or in the condensed phase in a physical or chemical mode or in combinations therein. The physical mode involves heat sinks, fuel diluents, or barrier formers, whereas the chemical mode affects the way the polymeric chains break down [17]. Laoutid et al. [18] underlined the role of char cohesiveness and mineral–polymer interactions in EVA/calcium-based minerals, which may affect the fire properties, accordingly. Wang et al. manufactured a multifunctional hybrid flame-retardant structure via the layer-by-layer assembly technique with brucite, silane coupling agents, nickel chloride, and sodium alginate, wherein the protective char layer played a decisive role in the enhanced fire performance, especially in combination with EVA [19]. Liu et al. exploited nanosized carbon black as a synergist in promoting char formation for improving the flame resistance of brucite in an EVA matrix, as this was manifested in LOI, UL94, and cone calorimetry testing [20]. In another example of advancing the flame retardancy of the EVA/PE matrix, Haurie et al. compounded organophilic montmorillonite, hydromagnesite, and aluminium hydroxide to benefit from their combined action [21].

Furthermore, carbonate minerals, which were long ago investigated for their flame retardancy [22], are recently attracting further attention again [7,23]. It has been reported that when calcium carbonate (CaCO_3) is employed as a filler in polymer matrices, the thermal and thermo-oxidative stability of the composite is improved [24]. Goodariz et al. reported an increase in the limiting oxygen index (LOI) of polypropylene (PP) from 17.4% to 23.6% for a 5 wt% CaCO_3 reinforced PP composite system [25]. The subject of the current analysis is to investigate the effect of carbonate mineral fillers on flame retardancy and dielectric properties in polar and non-polar polyolefin matrices.

2. Materials and Methods

Ethylene-1-octene copolymer (Lucene LC180) was supplied by LG Chemicals (Yeouidaero 128, Yeongdeungpo-gu Seoul, Korea). Ethylene–hexene copolymer (Exceed 3518) and olefinic elastomer (Vistamaxx 6202) were provided by Exxon Mobil Chemicals (Hermeslaan 2, 1831 Machelen, Belgium). Maleic anhydride modified polyethylene (Fusabond E226) was provided by Dow DuPont (2 Chemin du Pavillon Box 50, CH-1218 Le Grand

Saconnex Geneva, Switzerland). Ethylene vinyl acetate copolymer with 28 wt.% VA content (Greenflex FL65) was donated by Versalis (Piazza Boldrini 1, 20097 San Donato Milanese, Italy). Silicon lubricant (SilmaProcess AL1142A) was supplied by SILMA (Via A.Moro, 45 59016-Poggio a Caiano, Italy), and the antioxidant (Irganox 1010) was provided by BASF SE (38 Carl-Bosch Str., Ludwigshafen, Germany).

The selected minerals, which were mixed in the recipes, involve magnesium carbonate (magnesite— MgCO_3) (FlammaCarb 10A) with average particle size $d_{50} = 3.5 \mu\text{m}$, calcium carbonate ($\text{CaCO}_3 \geq 99\%$) with $d_{50} = 5.5 \mu\text{m}$, magnesium hydroxide (brucite— $\text{Mg}(\text{OH})_2$) with $d_{50} = 3.5 \mu\text{m}$, and hydrated magnesium–calcium carbonate (huntite/hydromagnesite mineral—HHM) with $d_{50} = 4.0 \mu\text{m}$. All minerals used were commercial products.

The ingredients for a polyethylene (PE recipe) and an ethylene vinyl acetate/polyethylene (EVA/PE recipe) compound are presented in Table 1.

Table 1. Ingredients of the polyethylene (PE) and ethylene vinyl acetate/polyethylene (EVA/PE) recipes in parts per hundred resin per weight (phr).

PE Recipe Ingredients	Dosage (phr)	EVA/PE Recipe Ingredients	Dosage (phr)
Lucene LC180	40	Greenflex FL65	60
Vistamaxx 6202	30	Lucene LC180	20
Exceed 3518	20	Exceed 3518	10
Fusabond E226	10	Fusabond E226	10
SilmaProcess		SilmaProcess	
AL1142A	3	AL1142A	3
Irganox 1010	0.5	Irganox 1010	0.5
Filler (various)	165	Filler (various)	165

The formulations, which are exploited in the current analysis, relate to halogen-free, flame-retardant cable compounds. The basic ingredient selection for such HFFR recipes includes minerals, compatibilizers, plasticizers, and antioxidants.

Mixing was performed in an internal mixer (Brabender Plastograph, Brabender GmbH & Co. KG, Kulturstr.49-51, 47055 Duisburg, Germany) at 180 °C, while the compounds were pressed in plates in a hot-press (Model 4122CE, Carver Inc.,1569 Morris Str., PO Box 544, Wabash, Indiana 46992-0544, USA) at 180 °C. Samples were cut with a pneumatic cutter (Pneumatic Die Cutter, Noselab ATS s.r.l., Via Garibaldi 144, 2080 Nova Milanese MB, Italy) at various dimensions according to the required standards and tests.

Scanning electron microscopy images were taken with an EVO MA 10 Zeis (ZEISS AG, Carl-Zeiss-Straße 22, 73447 Oberkochen, Germany). The melt flow index was measured in a melt flow tester (Noselab, ATS s.r.l. Via Garibaldi 144, 20834 Nova Milanese MB, Italy) at 190 °C and 21.6 kg according to ASTM D1238 [26]. Tensile tests were performed at 25 mm/min crosshead speed on a double-column machine (Model 10ST, Tinius Olsen Ltd, 6 Perrywood Business Park, Honeycrock Lane Salfords, Redhill, RH1 5DZ, UK) on dumb-bell specimens (ISO-37) [27] of 1 mm thickness. Thermogravimetric analysis (TGA) was conducted by employing a TA Q500 device (TA Instruments, New Castle, DE, USA) targeted to investigate the thermal degradation of the tested systems. Measurements were carried out from ambient temperature up to 900 °C with 10 °C/min heating rate in N_2 atmosphere. The dielectric response of the fabricated systems was examined by means of Broadband Dielectric Spectroscopy (BDS) by varying the frequency of the applied and the exerted temperature. The experimental set-up included an Alpha-N Frequency Response Analyzer, a Novotherm temperature controller, a BDS 1200 dielectric cell, and windeta software. Software and devices were all supplied by Novocontrol Technologies (Montabaur, Germany). Measurements were conducted in the frequency range of 10^{-1} to 10^7 Hz by applying a sinusoidal voltage across the specimen with $V_{\text{rms}} = 1$ V. Frequency scans were carried out under isothermal conditions, with the temperature varying from 30 to 100 °C

with step increments of 5 °C. The whole experimental procedure is in accordance with the ASTM D150 specifications [28].

Flammability was investigated by exploiting equipment for the limited oxygen index (Noselab) following ASTM D2863 and a fire testing cabinet (Noselab) for evaluation in UL 94 and ASTM D635 standards under vertical and horizontal configurations, respectively [29,30]. All specimens for fire testing were molded at the thickness of 3 mm.

3. Results

3.1. Fillers' Morphology

Figure 1 presents representative SEM images of the magnesium carbonate, calcium carbonate, brucite, and huntite/hydromagnesite minerals. The images reveal the shape of these inclusions, wherein a rather prismatic structure appears for the magnesium and the calcium carbonate, while a higher aspect ratio is observed for brucite and HHM fillers.

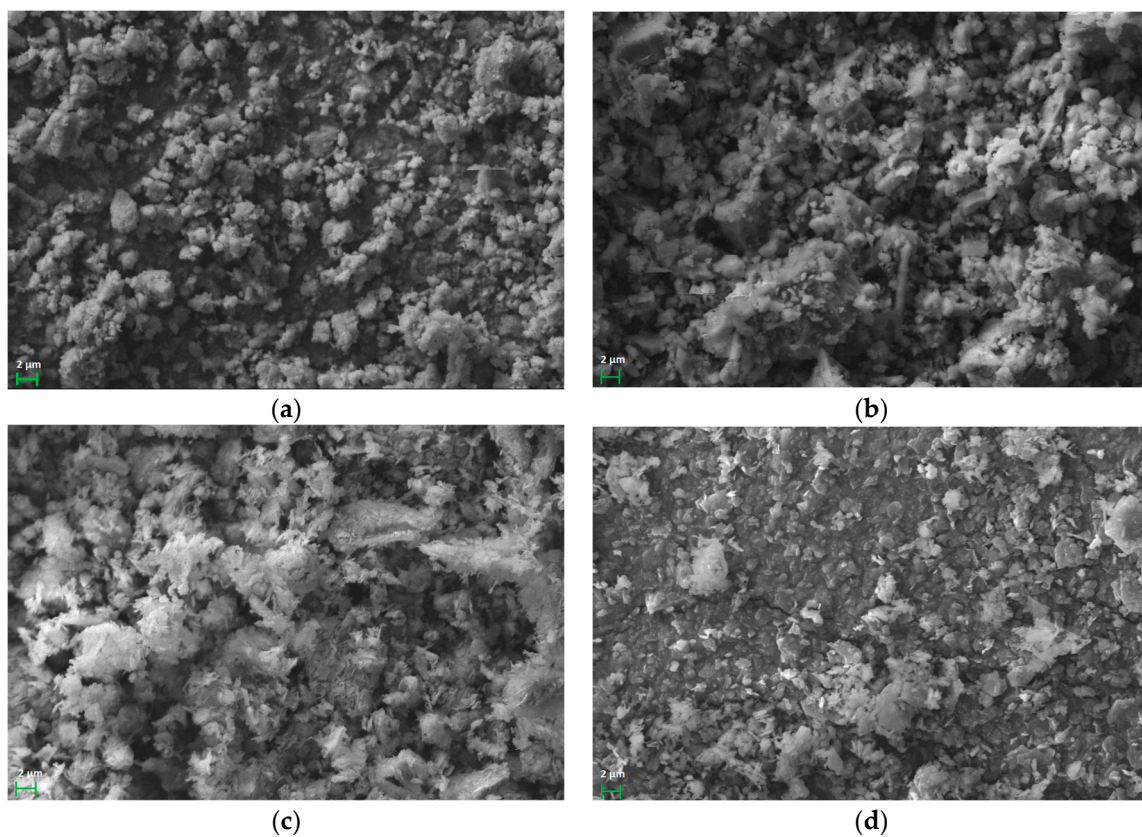


Figure 1. Scanning electron microscopy images of the minerals: (a) magnesium carbonate, (b) calcium carbonate, (c) magnesium hydroxide, and (d) huntite/hydromagnesite.

3.2. Rheological Properties

The high filler loading used in current recipes is expected to increase the melt viscosity [31]. Consequently, this would affect the torque values during polymer compounding and the measured melt flow index. As shown in Table 2, calcium carbonate presented the lowest torque and the highest melt flow index values, followed in performance by the magnesium carbonate. On the contrary, HHM and brucite presented increased melt viscosity, as this was revealed by their high torque and low melt flow index (MFI) values. The same pattern was followed in both polar and non-polar HFFR matrices used in current analysis.

Table 2. Torque at plateau and melt flow index of the compounds for the PE and EVA/PE recipes.

Filler Type	PE Recipe		EVA/PE Recipe	
	Torque at Plateau (N.m)	MFI 21.6 kg @ 190 °C (gr/10 min)	Torque at Plateau (N.m)	MFI 21.6 kg @ 190 °C (gr/10 min)
MgCO ₃	25.5	18.5	26.5	14.6
CaCO ₃	23.5	22.5	24.0	17.5
Mg(OH) ₂	30.0	13.2	35.5	9.2
HHM	27.5	14.0	29.0	8.3

The addition of EVA was found to increase the melt viscosity in the respective recipes. Such behavior would be expected for the high VA content used [32]. Nevertheless, for the calcium and the magnesium carbonate grades, the effect was limited, while HHM and brucite yielded the highest torque and MFI difference, respectively. As presented in Table 2, by shifting from the non-polar to the polar matrix, the brucite yielded an 18% increase in torque, while HHM calculated a 41% reduction in the MFI value.

Highly filled compounds are expected to present close particle packing, suggesting that the particle–particle interactions are predominant over the particle–matrix interactions [33]. The particle sizes of the mineral fillers used in the current analysis are of a similar average size (d_{50}); thus, the differences in their respective rheological performances, presented in Table 2, are related mainly to their surface hydroxyl or carbonate groups as well as their shape. The morphology of the minerals notably affects their rheological behavior, as the more spherical particles induce less disturbance to the flow compared to any other shape [34]. In practice, the difficulties of working with either magnesium hydroxide or HHM in such highly filled systems are overcome by using coatings like stearic acid, which renders said minerals hydrophobic [35].

3.3. Mechanical Properties

In cable compounds, the stress at break is expected to lay above 10 MPa combined with a high elongation at break [9]. In this view, all polymer HFFR composites showed an acceptable stress level, while the carbonate versions yielded the best strain at break percentages (Table 3). More specifically, the magnesium carbonate presented the highest elongation at break values in both polar and non-polar matrices. In general, the tensile performance of these compounds should be further improved during cable manufacturing. Cable extrusion induces an anisotropy in the extrudate, which enhances the mechanical performance at the longitudinal cable direction.

Table 3. Tensile performance of the PE and EVA/PE recipe composites.

Filler Type	PE Recipe		EVA/PE Recipe	
	Stress at Break (MPa)	Elongation at Break (%)	Stress at Break (MPa)	Elongation at Break (%)
MgCO ₃	10.9	137	12.3	161
CaCO ₃	10.0	116	10.1	112
Mg(OH) ₂	10.1	55	11.7	53
HHM	11.0	93	12.7	147

As shown in Table 3, the blending of EVA with PE rather improved the mechanical properties of the HFFR compounds. Property improvement through blending is often met in polymer blends [36]. The EVA's presence can affect the crystallization of PE [32] and enhance the dispersion of the filler in the polymeric matrix [37].

4. Discussion

The thermal stability of the polymer matrix in relation to the action of the different mineral fillers is outlined by the weight loss of each compound versus the temperature increase. As shown in Figure 2a, the weight loss of the PE matrix presents an abrupt single step degradation. This profile is changed by the incorporation of the mineral fillers within the non-polar polyethylene recipe, which results in multi-stage degradation schemes attributed to the decomposition temperatures of the various minerals [38]. This is especially apparent for the carbonate minerals, wherein their decomposition temperatures lay well above the degradation temperature of the polymer matrix. Likewise, as depicted in Figure 2b, the DTG peak of the matrix, which appears at 475.72 °C, remained rather unaffected by the addition of the mineral fillers. On the contrary, the HHM induced a slight peak shift at lower temperatures due to the early decomposition of hydromagnesite [39].

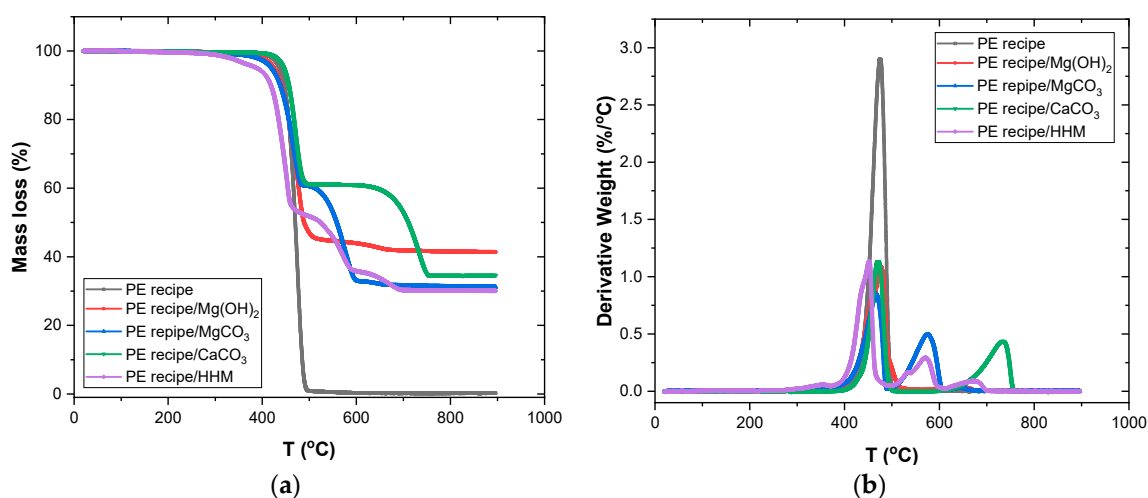


Figure 2. (a) Thermogravimetric analysis of the PE recipe matrix in comparison to the filled compounds. (b) Derivative of the thermogravimetric curve of the PE recipe matrix in comparison to the filled compounds.

The degradation profile of the compounds is changed drastically by the addition of EVA in the matrix. As shown in Figure 3a, the polar EVA/PE compound presents an early decomposition due to the deacetylation of the pendant acetate groups of EVA [40]. This specific degradation stage becomes smoother, and it is delayed by the incorporation of either the magnesium carbonate or the calcium carbonate. As shown in Figure 3b, the intensity of the first DTG peak for calcium and magnesium carbonate is significantly reduced, implying thermal stability improvement for these compounds. Magnesium hydroxide and huntite/hydromagnesite fillers also improved the thermal stability of the polar matrix, as this is identified by the shift at higher temperatures of the 5% weight loss onset by approximately 6.6 °C and 11.9 °C, respectively, although to a much smaller extent than the former carbonates.

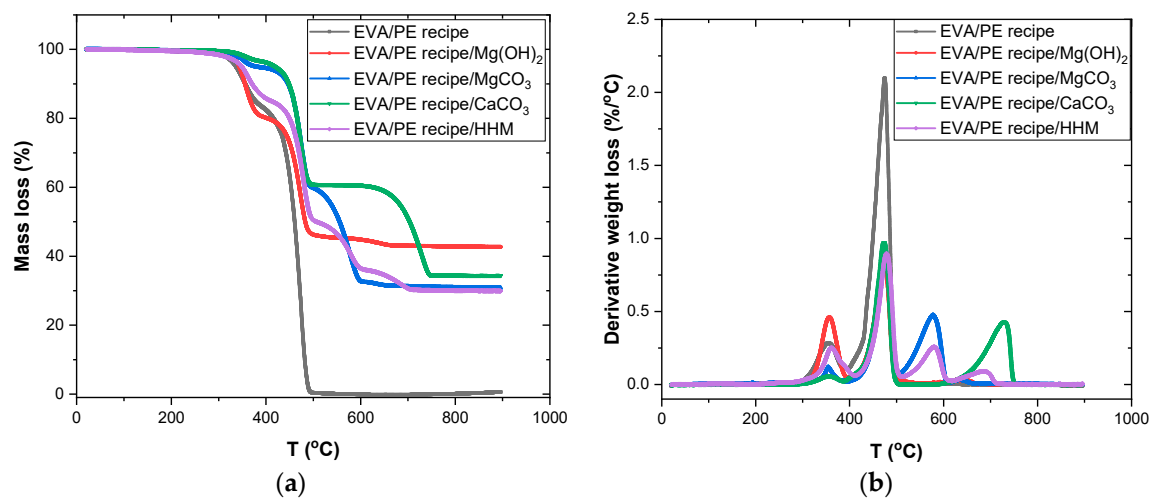


Figure 3. (a) Thermogravimetric analysis of the EVA/PE recipe matrix in comparison to the filled compounds. (b) Derivative of the thermogravimetric curve of the EVA/PE recipe matrix in comparison to the filled compounds.

Dielectric data can be analyzed by means of different formalisms, e.g., dielectric permittivity, electric modulus, and ac conductivity [41]. The dielectric quantity, which appears to be the most useful in engineering applications, is the real part of dielectric permittivity (ϵ'), sometimes still referred to as the dielectric constant, although it varies with the frequency of the applied field and the temperature. Figure 4a,b present the variation of the real part of dielectric permittivity with frequency, at 30 °C, for the PE and EVA/PE recipe-based composites. Filled polymers exhibit higher values of ϵ' in the whole frequency range. All four employed minerals at the reinforcing phase are semiconductive ceramics with higher permittivity than the polymer matrices, and their presence in the polymers leads to enhanced values of dielectric permittivity [42–45]. Moreover, the electrical characteristics (permittivity and conductivity) of the fillers vary from those of the matrices. Hence, the incorporation of fillers in the matrices introduces the effect of interfacial polarization (IP). IP is observed in heterogeneous systems via the accumulation of unbounded charges at the constituents' interface, where they form induced dipoles [41,44–47]. The influence of IP is more pronounced in the low frequency and high temperature range. Among the used fillers, HHM has the strongest effect upon the permittivity values for both types of matrices. Maximum values for ϵ' are recorded at the lowest measured frequency, which diminish with frequency. At the high frequency region, values of ϵ' , for all composites, acquire rather constant values, indicating only the effect of filler content, which remains rather constant in all cases. On the contrary, at the low frequency edge, the effect of the filler type becomes evident. According to the level of the introduced heterogeneity by each filler, composites exhibit higher values of dielectric permittivity. Heterogeneity and the resulting IP are strengthened as the difference between the products ($\epsilon'_f \cdot \sigma_f$) and ($\epsilon'_m \cdot \sigma_m$) becomes higher, where ϵ'_f , ϵ'_m , and σ_f , σ_m refer to the filler and the matrix permittivity and conductivity, respectively [41,48]. Induced dipoles at the interface are characterized by high inertia and fail to follow the alternation of the applied field as frequency increases, leading to lower values of ϵ' and the occurrence of relaxation processes. In addition, it should be noted that values of the real part of dielectric permittivity in the EVA/PE recipe systems are higher than the corresponding ones of the PE recipe matrix because of the polar nature of the EVA/PE recipe matrix.

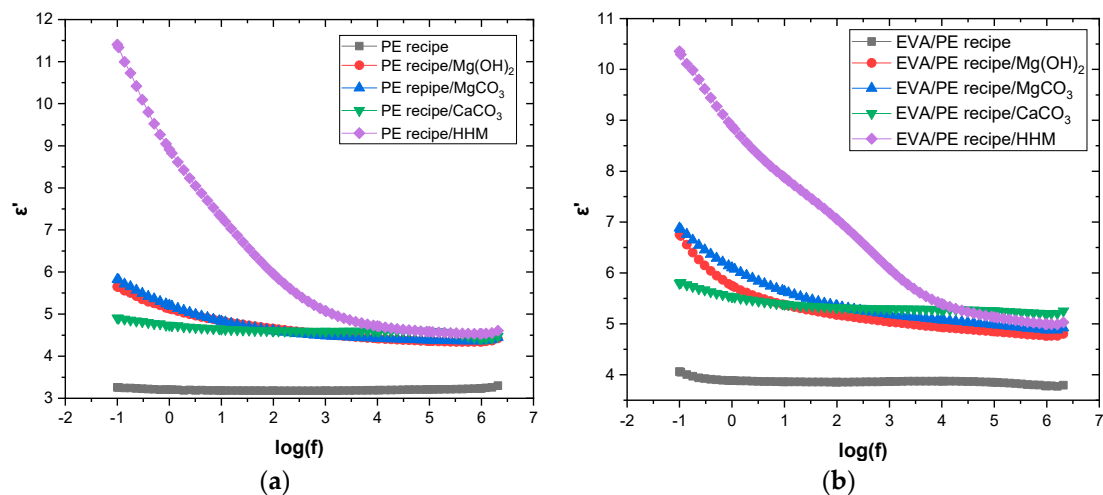


Figure 4. Variation of the real part of dielectric permittivity with frequency, at 30 °C, for the (a) PE recipe and (b) EVA/PE recipe-based systems.

Figure 5a,b depict the dependence of ϵ' on the temperature at 100 Hz. The influence of the filler type is evident in the whole temperature range. All reinforced systems exhibit enhanced values of the real part of dielectric permittivity relative to the corresponding matrices. Temperature seems not to significantly influence the permittivity values. A slight increase in ϵ' with temperature can be attributed to the increased mobility of dipoles, which is acquired by the thermal agitation, causing an enhancement in polarization. Systems with HHM display the highest values in the whole temperature range, for both types of matrices. The dielectric response of these composites appears to be more temperature dependent, as shown in the spectra of Figure 5a,b. This behavior could be related to the increased mobility of induced dipoles at the constituents' interface and/or to the difference in the thermal expansion coefficients between the filler and the matrices [41–43]. In addition, it is confirmed that the EVA/PE recipe systems exhibit higher values of the real part of dielectric permittivity when compared to the relative PE recipe systems.

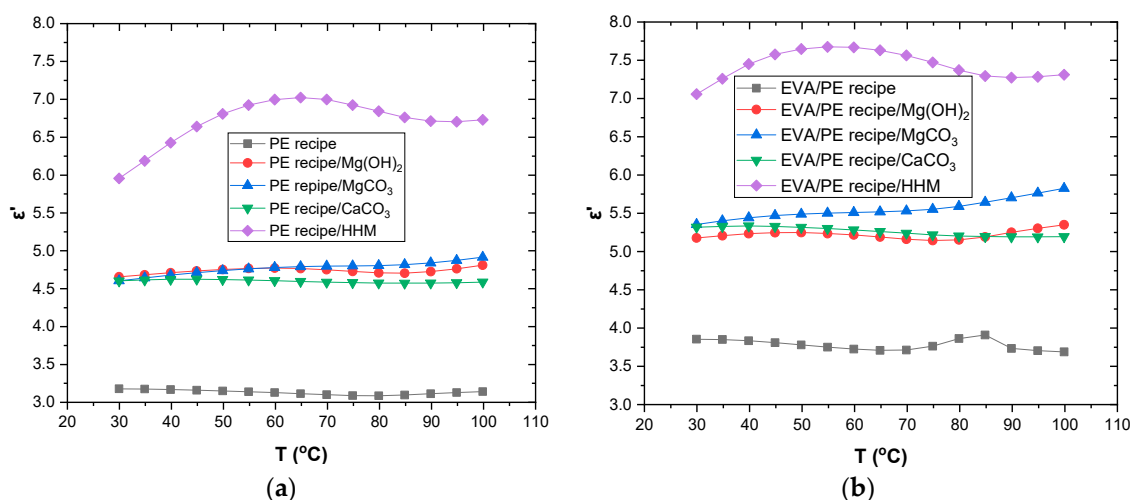


Figure 5. Variation of the real part of dielectric permittivity with temperature, at 100 Hz, for the (a) PE recipe and (b) EVA/PE recipe-based systems.

The effect of calcium and magnesium carbonate fillers on the flame resistance of the polyethylene matrix was alike, as shown in Table 4.

Table 4. Fire properties of the PE and EVA/PE recipe composites.

Filler Type	PE Recipe		EVA/PE Recipe	
	LOI (%)	UL 94 and ASTM D 635	LOI (%)	UL 94 and ASTM D 635
MgCO ₃	23.2	HB	31.0	HB
CaCO ₃	23.0	HB	26.2	HB
Mg(OH) ₂	31.0	HB	38.0	V-0
HHM	26.6	HB	30.0	HB

The critical decomposition temperatures of the minerals used differ from one another and relate to the points where abrupt weight loss in the respective TGA curves becomes apparent. As either water vapor or carbon dioxide is released during said mineral decomposition, the metal oxides left behind form a protective ceramic layer on the polymer surface, which blocks further heat transfer [49]. However, this char layer, when plain minerals are compounded without synergists, is usually fragile and allows for the migration of combustible volatiles. According to the literature, PE presents limited oxygen index (LOI) values around 17.5% [50,51]; thus, the non-polar matrix presented an improvement in LOI testing after the addition of all examined mineral fillers. Because magnesium carbonate decomposes around 500–550 °C [22], and calcium carbonate decomposes around 800–850 °C [52], it is considered that the improvement due to these carbonate minerals originates mostly from the significant reduction of the combustible polymeric components and less from their carbon dioxide emissions. In addition, mixing HHM induced a further LOI improvement, whereas brucite yielded an even better result. It seems that this performance for HHM and brucite in the PE compound additionally emanates from the H₂O release when said mineral fillers are decomposed after 220 °C and 300 °C, respectively [12,53,54]. Nevertheless, this was not manifested in UL 94 evaluation, where, in all cases, the polyethylene HFFR compounds failed to pass the vertical burning test. Similarly, during horizontal burning, all received the same HB characterization.

The differences in the measurement configuration among LOI and UL94 testing should be considered for evaluating the results. In the former case, the effect of dripping is negligible as the combustion progresses downwards, and flame dilatation acts synergistically with any endothermic decomposition phenomena. In the latter case, on the one hand, dripping acts decisively in the disqualification of the compound; on the other hand, the vertically upward flame propagation is diminished to a greater extent by the energy absorption through endothermic decomposition of the mineral rather than any flame dilution conditions [55]. Furthermore, the relatively high melt flow index of the PE compounds affected the burning performance of the relevant composites by supporting dripping during the UL94 testing.

The fire properties are significantly improved for all investigated minerals when EVA is added in the matrix. It must be mentioned that the LOI values of EVA in the literature appear to be close to 19% [56,57]. As depicted in Table 4, calcium carbonate presented the lowest improvement. On the contrary, magnesium carbonate had a notable performance in the presence of EVA, clearly surpassing that of calcium carbonate and resembling that of HHM. The polar nature of EVA composites, shown in Figures 4 and 5, introduces additional interactions between the matrix and the fillers' surface because of the presence of unbounded charges at the interface of the matrix/ceramic filler. In addition, the improved dispersion of the filler in the EVA/PE matrix led to an enhancement of FR properties. The magnesium hydroxide had the best performance in view of both LOI and UL 94 testing, achieving a V-0 characterization, wherein the self-sustaining combustion cycle of heat/fuel/oxygen was efficiently broken [58]. It seems that the increased flame retardancy of the EVA combined with the lower melt flow index of the respective compounds resulted in a better performance during the demanding UL94 testing. However, it was demonstrated that the ultimate performance (i.e., V-0) for the examined minerals in said test was achieved only in the case of magnesium hydroxide, wherein a further endothermic decomposition

with water vapor release shortly below the decomposition temperature of the matrix was in action.

It is known that EVA decomposes at two stages, namely around 350 °C, releasing acetic acid through decomposition of the vinyl acetate groups, and above 400 °C due to the thermal decomposition of the backbone [23,59]. It has been presented that hydroxides can interact with the acetic acid, which is released during the first stage of EVA degradation through acid–base chemistry [23]. Furthermore, magnesium oxide has a prominent role in enhancing char residue and in hindering dripping [60,61]. Therefore, brucite managed to deliver V-0 characterization under UL-94 testing in the EVA/PE formulation, surpassing the performance of the rest of the fillers. The amount of the carbon dioxide emitted during the decomposition of the carbonates also played its role in increasing the LOI values by diluting the flame. In general, such inert diluent gases may lower the concentration of the free radical, thus diminishing the fire [55]. In the case of magnesium carbonate, the amount of carbon dioxide release is greater than that emitted during the decomposition of the calcium carbonate. Nevertheless, the noticeable behavior of magnesium carbonate may relate to both the delay of deacetylation and the action of the formed magnesium oxide particles. This is an effective mechanism for improving flame retardancy [62]; however, alone, it was insufficient for passing the HFFR compound for the more demanding fire tests [63].

5. Conclusions

The current analysis compared the effect of calcium carbonate, magnesium carbonate, natural magnesium hydroxide, and huntite/hydromagnesite mineral fillers in non-polar (PE) and polar (EVA/PE) flame-retardant polymer compounds. It was found that the mineral additives significantly altered the mechanical, rheological, thermal, dielectric, and fire retardancy properties of the respective composites.

- Calcium and magnesium carbonates delivered the best rheological properties in terms of low torque during compounding and high MFI values.
- Magnesium carbonate resulted in the highest elongation at break in both polar and non-polar HFFR matrices.
- A remarkable thermal stability improvement was detected when EVA was combined with the carbonate minerals in the HFFR compounds.
- The real part of the dielectric permittivity has been increased through the addition of EVA, while the maximum values for ϵ' are recorded at the lowest measured frequency, especially for the HHM mineral, due to its morphology and induced electrical heterogeneity.
- The addition of EVA in the polymer recipe improved the flame resistance in all examined fillers, wherein mineral magnesium hydroxide presented the best fire resistance and magnesium carbonate showed a notable synergistic action with the EVA matrix. The developed composites could meet the requirements of applications like, for example, the construction or the electrical/electronic sectors, wherein there are various classifications in the European regulations according to the respective fire growth rate of the composites [64].

Author Contributions: For conceptualization, methodology, and validation, K.G.G., A.C.P., and G.C.P. are responsible; formal analysis, investigation, and data curation were conducted by K.G.G., N.A., A.C.P., and G.C.P.; writing—original draft preparation, K.G.G., A.C.P., and G.C.P.; writing—review and editing, K.G.G., A.C.P., and G.C.P.; supervision and project administration, K.G.G. and G.C.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are available upon request.

Conflicts of Interest: Authors Konstantinos G. Gatos and Nikolaos Apostolopoulos were employed by the company Terna Mag S.A. The remaining authors declare that the research was conducted

in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Arao, Y. Flame Retardancy of Polymer Nanocomposite. In *Flame Retardants Polymer Blends, Composites and Nanocomposites*; Visakh, P.M., Arao, Y., Eds.; Springer: Berlin/Heidelberg, Germany, 2015; pp. 15–44.
2. Bar, M.; Alagirusamy, R.; Das, A. Flame Retardant Polymer Composites. *Fibers Polym.* **2015**, *16*, 705–717. [\[CrossRef\]](#)
3. Ilyas, R.A.; Sapuan, S.M.; Asyraf, M.R.M.; Norrrahim, M.N.F.; Dayana, D.A.Z.N.; Amelia, J.J.N.; Rani, M.S.A.; Nurazzi, N.M.; Aisyah, H.A.; Sharma, S.; et al. Polymer Composites Filled with Metal Derivatives: A Review of Flame Retardants. *Polymers* **2021**, *13*, 1701. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Shen, J.; Liang, J.; Lin, X.; Lin, H.; Yu, J.; Wang, S. The Flame-Retardant Mechanisms and Preparation of Polymer Composites and Their Potential Application in Construction Engineering. *Polymers* **2022**, *14*, 82. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Innes, J.; Innes, A. *Plastic Flame Retardants: Technology and Current Developments*; Rapra: Shropshire, UK, 2003; pp. 14–16.
6. Sauerwein, R. Mineral filler flame retardants. In *Non-Halogenated Flame Retardant Handbook*; Morgan, A.B., Wilkie, C.A., Eds.; Wiley: Hoboken, NJ, USA, 2014; pp. 75–141.
7. Samoylenko, D.E.; Rodygin, K.S.; Ananikov, V.P. Sustainable application of calcium carbide residue as a filler for 3D printing materials. *Sci. Rep.* **2023**, *13*, 4465. [\[CrossRef\]](#)
8. Banks, J.D.; Emami, A. Carbon-based piezoresistive polymer nanocomposites by extrusion additive manufacturing: Process, material design, and current progress. *3d Print. Addit. Manuf.* **2024**, *11*, e548–e571. [\[CrossRef\]](#)
9. Sener, A.A.; Demirhan, E. The investigation of using magnesium hydroxide as a flame retardant in the cable insulation material by cross-linked polyethylene. *Mater. Des.* **2008**, *29*, 1376–1379. [\[CrossRef\]](#)
10. Hollingbery, L.A.; Hull, T.R. The fire retardant effects of huntite in natural mixtures with hydromagnesite. *Polym. Degrad. Stab.* **2012**, *97*, 504–512. [\[CrossRef\]](#)
11. Haveriku, S.; Meucci, M.; Badalassi, M.; Cardelli, C.; Ruggeri, G.; Pucci, A. Optimization of the mechanical properties of polyolefin composites loaded with mineral fillers for flame retardant cables. *Micro* **2021**, *1*, 102–119. [\[CrossRef\]](#)
12. Hollingbery, L.A.; Hull, T.R. The thermal decomposition of huntite and hydromagnesite—A review. *Thermochim. Acta* **2010**, *509*, 1–11. [\[CrossRef\]](#)
13. McGary, K.; Zilberman, J.; Hull, T.R.; Woolley, W.D. Decomposition and combustion of EVA and LDPE alone and when fire retardant with ATH. *Polym. Int.* **2000**, *49*, 1193–1198. [\[CrossRef\]](#)
14. Rothon, R.N.; Hornsby, P.R. Flame retardant effects of magnesium hydroxide. *Polym. Degrad. Stab.* **1996**, *54*, 383–385. [\[CrossRef\]](#)
15. Laoutid, F.; Bonnaud, L.; Alexandre, M.; Lopez-Cuesta, J.-M.; Dubois, P. New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. *Mater. Sci. Eng. R Rep.* **2009**, *63*, 100–125. [\[CrossRef\]](#)
16. Levchik, S.V. Introduction to Flame Retardancy and Polymer Flammability. In *Flame Retardant Polymer Nanocomposites*; Morgan, A.B., Wilkie, C.A., Eds.; Wiley: Hoboken, NJ, USA, 2007; pp. 1–29.
17. Weil, E.D.; Levchik, S.V. *Flame Retardants for Plastics and Textiles*; Hanser: Munich, Germany, 2009; pp. 241–251.
18. Laoutid, F.; Lorgouilloux, M.; Lesueur, D.; Bonnaud, L.; Dubois, P. Calcium-based hydrated minerals: Promising halogen-free flame retardant and fire resistance additives for polyethylene and ethylene vinyl acetate copolymers. *Polym. Degrad. Stab.* **2013**, *98*, 1617–1625. [\[CrossRef\]](#)
19. Wang, Y.; Yang, X.; Peng, Y.; Wang, F.; Liu, X.; Yang, Y.; Hao, J. Layer-by-layer assembly of multifunctional flame retardant based on brucite, 3-aminopropyltriethoxysilane, and alginate and its applications in ethylene-vinyl acetate resin. *ACS Appl. Mater. Interfaces* **2016**, *8*, 9925–9935. [\[CrossRef\]](#) [\[PubMed\]](#)
20. Liu, Z.; Zhang, Y.; Li, N.; Wen, X.; Nogales, L.A.; Li, L.; Guo, F. Study of nanocarbon black as synergist on improving flame retardancy of ethylene-vinyl acetate/brucite composites. *J. Therm. Anal. Calorim.* **2019**, *136*, 601–608. [\[CrossRef\]](#)
21. Haurie, L.; Fernández, A.I.; Velasco, J.I.; Chimenos, J.M.; Lopez Cuesta, J.-M.; Espiell, F. Thermal stability and flame retardancy of LDPE/EVA blends filled with synthetic hydromagnesite/aluminium hydroxide/montmorillonite and magnesium hydroxide/aluminium hydroxide/montmorillonite mixtures. *Polym. Degrad. Stab.* **2007**, *92*, 1082–1087. [\[CrossRef\]](#)
22. Rigolo, M.; Woodhams, R.T. Basic magnesium carbonate flame retardants for polypropylene. *Polym. Eng. Sci.* **1992**, *32*, 327–334. [\[CrossRef\]](#)
23. Laoutid, F.; Vahabi, H.; Movahedifar, E.; Laheurte, P.; Vagner, C.; Cochez, M.; Brison, L.; Saeb, M.R. Calcium carbonate and ammonium polyphosphate flame retardant additives formulated to protect ethylene vinyl acetate copolymer against fire: Hydrated or carbonated calcium? *J. Vinyl Addit. Technol.* **2021**, *27*, 264–274. [\[CrossRef\]](#)
24. Zhu, J.; Uhl, F.M.; Morgan, A.B.; Wilkie, C.A. Studies on the mechanism by which the formation of nanocomposites enhances thermal stability. *Chem. Mater.* **2001**, *13*, 4649–4654. [\[CrossRef\]](#)
25. Goodarzi, V.; Monemian, S.A.; Angaji, M.T.; Motahari, S. Improvement of thermal and fire properties of polypropylene. *J. Appl. Polym. Sci.* **2009**, *110*, 2971–2979. [\[CrossRef\]](#)
26. ASTM D1238-10; Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer, American Society for Testing Materials. ASTM International: West Conshohocken, PA, USA, 2013.
27. ISO-37:2024; Rubber, vulcanized or thermoplastic — Determination of tensile stress-strain properties, Standards catalogue, ICS, 83, 83.060. ISO: Geneva, Switzerland, 2024.

28. ASTM D150-18; Standard Test Methods for AC Loss Characteristics and Permittivity (Dielectric Constant) of Solid Electrical Insulation, American Society for Testing Materials. ASTM International: West Conshohocken, PA, USA, 2022.
29. ASTM D2863-19; Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index), American Society for Testing Materials. ASTM International: West Conshohocken, PA, USA, 2023.
30. ASTM D635-22; Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Plastics in a Horizontal Position. ASTM International: West Conshohocken, PA, USA, 2022.
31. Gao, Y.; Wang, Q.; Qiu, L.; Wu, J.; Yan, X.; Umar, A.; Guo, J.; Zhang, X.; Wang, J.; Guo, Z. Ethylene-vinyl acetate/LDH nanocomposites with enhanced thermal stability, flame retardancy, and rheological property. *Polym. Compos.* **2016**, *37*, 3449–3459. [\[CrossRef\]](#)
32. Farias, G.M.G.; Agrawal, P.; Hanken, R.B.L.; de Araújo, J.P.; de Oliveira, A.D.B.; de Mélo, T.J.A. Effect of EVA copolymer containing different VA content on the thermal and rheological properties of bio-based high-density polyethylene/ethylene vinyl acetate blends. *J. Therm. Anal. Calorim.* **2021**, *146*, 2127–2139. [\[CrossRef\]](#)
33. Rueda, M.M.; Auscher, M.-C.; Fulchiron, R.; Périé, T.; Martin, G.; Sonntag, P.; Cassagnau, P. Rheology and applications of highly filled polymers: A review of current understanding. *Prog. Polym. Sci.* **2017**, *66*, 22–53. [\[CrossRef\]](#)
34. Barnes, H.A. A review of the rheology of filled viscoelastic systems. *Rheol. Rev.* **2003**, 1–36.
35. Focke, W.W.; Molefe, D.; Labuschagne, F.J.W.; Ramjee, S. The influence of stearic acid coating on the properties of magnesium hydroxide, hydromagnesite, and hydrotalcite powders. *J. Mater. Sci.* **2009**, *44*, 6100–6109. [\[CrossRef\]](#)
36. Gatos, K.G. Natural rubber based polar synthetic rubber blends. In *Natural Rubber Materials*; Thomas, S., Chan, C.H., Pothen, L.A., Rajisha, K.R., Maria, H.J., Eds.; The Royal Society of Chemistry: Cambridge, UK, 2014; pp. 213–241.
37. Entezam, M.; Nozari, D.; Mirjalili, M.; Khonakdar, H.A. On the melt rheological behavior and microstructure of nanoclay-filled polyethylene/ethylene vinyl acetate (PE/EVA) blend. *Polym.-Plast. Technol. Eng.* **2015**, *54*, 1571–1584. [\[CrossRef\]](#)
38. Yücesoy, A.; Balçık Tamer, Y.; Berber, H. Improvement of flame retardancy and thermal stability of highly loaded low density polyethylene/magnesium hydroxide composites. *J. Appl. Polym. Sci.* **2023**, *140*, e54107. [\[CrossRef\]](#)
39. Andrikopoulos, K.S.; Bounos, G.; Lainioti, G.C.; Ioannides, T.; Kallitsis, J.K.; Voyiatzis, G.A. Flame retardant nano-structured fillers from huntite/hydromagnesite minerals. *Nanomaterials* **2022**, *12*, 2433. [\[CrossRef\]](#)
40. El-Taweel, S.H. Synergistic effect of -TiO_2 nanoparticles and poly (ethylene co vinyl acetate) on the morphology and crystallization behavior of polylactic acid. *Sci. Rep.* **2024**, *14*, 18142. [\[CrossRef\]](#)
41. Psarras, G.C. Conductivity and dielectric characterization of polymer nanocomposites. In *Physical Properties and Applications of Polymer Nanocomposites*; Tjong, S.C., Mai, Y.-M., Eds.; Woodhead Publishing: Cambridge, UK, 2010; pp. 31–69.
42. Sanida, A.; Stavropoulos, S.G.; Speliotis, T.; Psarras, G.C. Development, characterization, energy storage and interface dielectric properties in $\text{SrFe}_{12}\text{O}_{19}$ /epoxy nanocomposites. *Polymer* **2017**, *120*, 73–81. [\[CrossRef\]](#)
43. Koufakis, E.; Mathioudakis, G.N.; Patsidis, A.C.; Psarras, G.C. ZnTiO_3 /epoxy resin nanocomposites: Development, dielectric behaviour and functionality. *Polym. Test.* **2019**, *77*, 105870. [\[CrossRef\]](#)
44. Blatsi, C.; Patsidis, A.C.; Psarras, G.C. Dielectric Properties and Energy Storage of Hybrid/Boron Nitride/Titanium Carbide/Epoxy Nanocomposites. *J. Compos. Sci.* **2022**, *6*, 259. [\[CrossRef\]](#)
45. Patsidis, A.C.; Koufakis, E.; Mathioudakis, G.N.; Vryonis, O.; Psarras, G.C. Development, Dielectric Response, and Functionality of ZnTiO_3 / BaTiO_3 /Epoxy Resin Hybrid Nanocomposites. *J. Compos. Sci.* **2024**, *8*, 225. [\[CrossRef\]](#)
46. Gioti, S.; Sanida, A.; Mathioudakis, G.N.; Patsidis, A.C.; Speliotis, T.; Psarras, G.C. Multitasking Performance of Fe_3O_4 / BaTiO_3 /Epoxy Resin Hybrid Nanocomposites. *Materials* **2022**, *15*, 1784. [\[CrossRef\]](#)
47. Manika, G.C.; Gioti, S.; Sanida, A.; Mathioudakis, G.N.; Abazi, A.; Speliotis, T.; Patsidis, A.C.; Psarras, G.C. Multifunctional Performance of Hybrid $\text{SrFe}_{12}\text{O}_{19}$ / BaTiO_3 /Epoxy Resin Nanocomposites. *Polymers* **2022**, *14*, 4817. [\[CrossRef\]](#)
48. Mathioudakis, G.N.; Patsidis, A.C.; Psarras, G.C. Dynamic electrical thermal analysis on zinc oxide/epoxy resin nanodielectrics. *J. Therm. Anal. Calorim.* **2014**, *116*, 27–33. [\[CrossRef\]](#)
49. Lei, Y.; Zhao, X.; Xu, L.; Li, H.; Liang, J.; Yeoh, G.H.; Wang, W. Natural flame retardant minerals for advanced epoxy composites. *Fire* **2024**, *7*, 308. [\[CrossRef\]](#)
50. Hu, X.-P.; Li, Y.-L.; Wang, Y.-Z. Synergistic effect of the charring agent on the thermal and flame retardant properties of polyethylene. *Macromol. Mater. Eng.* **2004**, *289*, 208–212. [\[CrossRef\]](#)
51. Gul, R.; Islam, A.; Yasin, T.; Mir, S. Flame-retardant synergism of sepiolite and magnesium hydroxide in a linear low-density polyethylene composite. *J. Appl. Polym. Sci.* **2011**, *121*, 2772–2777. [\[CrossRef\]](#)
52. Hapuarachchi, T.D.; Peijs, T. Aluminium trihydroxide in combination with ammonium polyphosphate as flame retardants for unsaturated polyester resin. *Express Polym. Lett.* **2009**, *3*, 743–751. [\[CrossRef\]](#)
53. Miyata, S.; Imahashi, T.; Anabuki, H. Fire-retarding polypropylene with magnesium hydroxide. *J. Appl. Polym. Sci.* **1980**, *25*, 415–425. [\[CrossRef\]](#)
54. Savas, L.A.; Arslan, C.; Hacioglu, F.; Dogan, M. Effect of reactive and nonreactive surface modifications and compatibilizer use on mechanical and flame-retardant properties of linear low-density polyethylene filled with huntite and hydromagnesite mineral. *J. Therm. Anal. Calorim.* **2018**, *134*, 1657–1666. [\[CrossRef\]](#)
55. Hull, T.R.; Witkowski, A.; Hollingbery, L. Fire retardant action of mineral fillers. *Polym. Degrad. Stab.* **2011**, *96*, 1462–1469. [\[CrossRef\]](#)

56. Yu, L.; Chen, L.; Dong, L.-P.; Li, L.-J.; Wang, Y.-Z. Organic-inorganic hybrid flame retardant: Preparation, characterization and application in EVA. *RSC Adv.* **2014**, *4*, 17812–17821. [[CrossRef](#)]
57. Yen, Y.-Y.; Wang, H.-T.; Guo, W.-J. Synergistic flame retardant effect of metal hydroxide and nanoclay in EVA composites. *Polym. Degrad. Stab.* **2012**, *97*, 863–869. [[CrossRef](#)]
58. Gatos, K.G. Flame retardant properties of biocomposites for aircraft applications. In *Biocomposites for Industrial Applications*; Muthukumar, C., Thiagamani, S.M.K., Krishnasamy, S., Parameswaranpillai, J., Siengchin, S., Eds.; Woodhead Publishing: Cambridge, UK, 2024; pp. 255–273.
59. Beyer, G. Flame retardancy of nanocomposites—From research to technical products. *J. Fire Sci.* **2005**, *23*, 75–87. [[CrossRef](#)]
60. Ma, Z.-L.; Fan, C.-R.; Lu, G.-Y.; Liu, X.-Y.; Zhang, H. Synergy of magnesium and calcium oxides in intumescent flame-retardant polypropylene. *J. Appl. Polym. Sci.* **2012**, *125*, 3567–3574. [[CrossRef](#)]
61. Lin, M.; Li, B.; Li, Q.; Li, S.; Zhang, S. Synergistic effect of metal oxides on the flame retardancy and thermal degradation of novel intumescent flame-retardant thermoplastic polyurethanes. *J. Appl. Polym. Sci.* **2011**, *121*, 1951–1960. [[CrossRef](#)]
62. Hewitt, F.; Rhebat, D.E.; Witkowski, A.; Hull, T.H. An experimental and numerical model for the release of acetone from decomposition EVA containing aluminium, magnesium or calcium hydroxide flame retardants. *Polym. Degrad. Stab.* **2016**, *127*, 65–78. [[CrossRef](#)]
63. Morgan, A.B.; Cogen, J.M.; Opperman, R.S.; Harris, J.D. The effectiveness of magnesium carbonate-based flame retardants for poly(ethylene-co-vinyl acetate) and poly(ethylene-co-ethyl acrylate). *Fire Mater.* **2007**, *31*, 387–410. [[CrossRef](#)]
64. Schartel, B.; Kebelmann, K. Fire testing for the development of flame retardant polymeric materials. In *Flame Retardant Polymeric Materials, a Handbook*; Hu, Y., Wang, X., Eds.; CRC Press: London, UK, 2020; pp. 35–55.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.