

Research Article

Effect of Nanometric Metallic Hydroxides on the Flame Retardant Properties of HDPE Composites

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The effect of nanometric magnesium and aluminum hydroxides on the flame retardancy of high density polyethylene was studied. Additionally, the effect of maleic anhydride grafted polyethylene (PEgMA) and methyl acrylate grafted polyethylene (EMA) compatibilizers, on the tensile properties, was also studied. Morphological characterization of nanocomposites was carried out by means of scanning transmission electron microscopy (STEM). Flame retardant properties of nanocomposites were evaluated by the UL-94 horizontal and vertical tests as well as by cone calorimeter tests. Thermal degradation behavior was analyzed with a thermogravimetric analyzer (TGA). Tensile tests were carried out according to ASTM D 638-03 in an Instron 4301 tensile testing machine. From STEM images, a good dispersion of flame retardants (MH and ATH) in the polymer matrix was observed, which was reflected in the flame retardant properties. Results showed that the combination of nanometric MH and ATH produced excellent flame retardant properties, achieving a classification of V0 in the UL-94-V test and producing the lowest peak of heat release rate (PHRR) and the lowest total heat released (THR) in the cone calorimeter test. Finally, the addition of compatibilizer, especially PEgMA, resulted in much better tensile properties as compared to the noncompatibilized composition, maintaining the flame retardant properties.

1. Introduction

Polyethylene (PE) is used in many different applications, due to its good all-around properties. Polyethylene, however, has a serious limitation when flame resistance is of importance in a given application. To overcome this limitation, flame retardants are added to the PE composition. After the highly efficient halogen-containing flame retardants have been banned, some fairly efficient halogen-free flame retardants are the hydrated metallic hydroxides [1–3].

Metallic hydroxide flame retardants comprise a large volume flame retardant group in the polymers market today. This group of products also presents no risk to human health or the environment and can therefore be labelled as environmentally friendly. These include aluminum hydroxide

(ATH), magnesium hydroxide (MH), and a few other less common like magnesium-aluminium hydroxyl carbonates and certain other mixed metal hydroxides. However, ATH and MH together comprise most of the market volume of these flame retardants.

These metallic hydroxides reduce the flammability of polyethylene compositions, though high hydroxide content has to be used in order to attain acceptable flame retardancy. This high filler loading has a negative effect on several mechanical properties, turning the PE into a brittle and fragile composition with very poor tensile and impact properties.

ATH provides a flame retardant effect as it decomposes endothermically ($\Delta H -280$ cal/g) [4] into aluminum oxide and water (about 35 wt%). MH also decomposes endothermically ($\Delta H -328$ cal/g) [4] into magnesium oxide

TABLE 1: Compositions studied (*all amounts are in phr; parts per hundred parts of resin*).

Compositions ^{a,b}	HDPE	EPDM	MH	ATH	MH	ATH
			μm		nm	
M1	90	10	—	—	130	—
M2	90	10	32	—	98	—
M3	90	10	65	—	65	—
M4	90	10	98	—	32	—
M5	90	10	130	—	—	—
A1	90	10	—	—	—	130
A2	90	10	—	32	—	98
A3	90	10	—	65	—	65
A4	90	10	—	98	—	32
A5	90	10	—	130	—	—
MA2	90	10	—	—	98	32
MA3	90	10	—	—	65	65
MA4	90	10	—	—	32	98

^aAll compositions contain 0.2 phr silicon lubricant plus 0.15 phr antioxidant.

^bM compositions with micro- and nano-MH. A compositions with micro- and nano-ATH.

MA compositions with mix of nano-MH and nano-ATH.

and water (about 31 wt%). These decomposition reactions absorb heat from the combustion zone, but, in addition, the resulting metallic oxide is left behind and provides a protective intumescent layer on the surface of the substrate. The decomposition temperature of ATH [5, 6] begins at ca. 240°C, which may limit its application to polymers processed at relatively low temperatures, such as polyethylene, whereas MH begins to decompose at 320°C and allows its application to a much wider range of polymers.

To this end, there are a number of reports which consider the application of magnesium hydroxide nanoparticles as flame retardants in polymers [7, 8].

In 2003, at the ninth European Meeting on the Fire Retardancy of Polymeric Materials, several papers were focused on either micro- or nanomineral additives, such as aluminum hydroxide and magnesium hydroxide.

A comparison of Limiting Oxygen Index (LOI) and tensile strength (TS) data for EVA/MH composites, using micro- and nanosize MH, showed that TS of the microcomposites decreased with increasing filler level, whereas it was almost unaffected on the nanocomposites [9, 10]. LOI results for the nano-MH were also superior, especially at high filler levels. However, it should be noted that high nano-MH levels were still required to achieve reasonable resistance to ignition in common with more conventional, microsize, MH fillers. This negative effect on the mechanical properties is mainly due to the lack of interactions and/or compatibility between the highly nonpolar polymer matrix and the polar filler particles. One way to promote these interactions and/or compatibility is through the addition of a coupling agent, such as silanes [9], or, alternatively, through the addition of a compatibilizing agent, that is, a polymer combining the polar (hydrophilic) and nonpolar (hydrophobic) characteristics

such as maleic anhydride grafted polyethylene (PEgMA) [10–13] or copolymers of ethylene with butyl acrylate (EBA) or methyl acrylate (EMA) [13, 14].

It is the purpose of this work to study the effect of nanometric metallic hydroxides in combination with compatibilizing agents upon the fire retardancy and mechanical properties of polyethylene nanocompounds.

2. Experimental

2.1. Materials. Materials used were micrometric magnesium hydroxide (MH) from Nuova Sima, Italy, with particle size of 2.4 μm , aluminum hydroxide (ATH) from Albemarle, USA, with particle size of 1.2 μm , and nanometric MH and ATH from Nanostructured & Amorphous Materials, USA, with particle size of 20 and 50 nm, respectively. A thermal stabilizer (BNX1035) and silicon oil (Wacker AK1000) were also used. The high density polyethylene (HDPE) used was from Dow Chemical, USA, with MFI of 0.7 g/10 min (at 190°C with 2.16 kg), density of 0.954 g/cm³, and fusion temperature (T_m) of 127°C. The modified polyethylenes used as compatibilizers were from Arkema, USA, a maleic anhydride grafted polyethylene (PEgMA) with 2 wt% of maleic anhydride, with MFI of 3.5 g/10 min, and methyl acrylate grafted polyethylene (EMA) with 18 wt% methyl acrylate, with MFI of 2.5 g/10 min. For compound softness, an Ethylene-Propylene-Diene rubber (EPDM), from Lyondell, USA, with 70 wt% ethylene, with MFI of 0.6 g/10 min was used.

2.2. Mixing and Sample Preparation. The formulations initially prepared are described in Table 1. Each composition was first mixed in a Henschel intensive powder mixer for 10 min,

TABLE 2: Flame resistance and tensile properties of compositions presented in Table 1.

Formulations	Flame resistance		Stress [MPa]	Tensile properties	
	UL-94-V	UL-94-HB		Elongation [%]	Modulus [MPa]
HDPE	Fails, drips	Fails	16.0 ± 1.0	500 ± 40	340 ± 35
M1	Fails, drips	AE ^c	14.8 ± 0.6	50 ± 5	510 ± 45
M2	Fails, drips	AE	14.9 ± 0.8	40 ± 5	510 ± 50
M3	Fails, drips	AE	14.5 ± 0.5	50 ± 4	495 ± 50
M4	Fails, drips	AE	14.6 ± 0.8	40 ± 4	515 ± 45
M5	Fails, drips	AE	14.5 ± 0.6	50 ± 5	505 ± 55
A1	Fails, drips	AE	12.2 ± 0.6	50 ± 6	490 ± 40
A2	Fails, drips	AE	11.9 ± 0.6	40 ± 5	495 ± 45
A3	Fails, drips	AE	12.2 ± 0.8	40 ± 5	480 ± 45
A4	Fails, drips	AE	11.9 ± 1.0	40 ± 4	500 ± 55
A5	Fails, drips	AE	12.4 ± 1.0	40 ± 4	500 ± 50
MA2	Fails, drips	AE	14.9 ± 1.0	50 ± 5	500 ± 50
MA3	V1	AE	14.2 ± 0.8	50 ± 5	505 ± 45
MA4	Fails, drips	AE	14.2 ± 1.0	50 ± 4	490 ± 50

^cAutoextinguishable.

at 50°C and 1000 rpm. Thereafter, the dry mix was fed into a Werner ZSK30 corotating twin screw extruder with L/D of 29 and D of 30 mm, at 100 rpm.

It should be noted that when avoiding the use of halogenated compounds, very high levels of flame retardant additive, such as MH, are required to achieve reasonable fire resistance. This is the reason for using up to 130 phr of flame resistance additive.

Compositions with MH were processed at 205°C, whereas those with ATH were processed at 170°C. Compositions with a mix of magnesium and aluminum hydroxides were processed at 170°C. Immediately after extrusion, the materials were passed through a two-roll mill, at 150°C the ones with MH and at 135°C those with ATH, to obtain small “bands” of each composition. Finally, the compositions were compression molded, at 190°C the ones with MH and at 170°C those with ATH, to obtain 125 × 125 × 3 mm laminates from which test specimens were cut.

2.3. Characterization. The UL 94 test is perhaps the most frequently used small flame burner test. It provides an assessment of flammability for a variety of thermoplastic materials intended for use in multiple applications. Performance is described through one of three ratings, V0, V1, or V2, depending on the number of seconds of after-flame burn time for each specimen, the total after-flame burn time for all specimens, the afterglow time, and the existence of flaming particles which may ignite a piece of cotton placed beneath the test specimens.

Flammability tests were performed according to UL-94, in both vertical (94 V) and horizontal (94 HB) arrangements, on 125 × 13 × 3 mm specimens cut from compression molded laminates, which were previously conditioned for 48 h at 23°C and 50% RH.

Flammability tests were additionally performed on an FTT Dual Cone Calorimeter under a heat flux of 35 kW/m², in accordance with ASTM E1354, on 100 × 100 mm specimens. Before testing, all specimens were conditioned for 24 hours at 23 ± 3°C and 50 ± 5% RH and then wrapped with aluminum foil around the back and edges, to prevent molten material to drip over the load cell. The test samples were finally backed with a noncombustible insulating material and tested. All samples were run in triplicate.

Tensile tests were carried out according to ASTM D 638-03 in an Instron 4301 tensile testing machine at a deformation rate of 5 mm/min.

Thermogravimetric analyses were performed in a TA Instruments TGA-951 between 30 and 600°C, using a heating rate of 10°C/min, under a nitrogen flow of 50 mL/min.

The Melt Flow Index (MFI) tests for pure HDPE and HDPE composites were carried out at 190°C, under a 2.16 kg weight, according to ASTM D1238.

Morphology and nanoparticle dispersion analyses were carried out with a JEOL JSM-7401 scanning electron microscope in transmission mode (STEM), on Au-Pd coated fractured samples from the previously obtained laminates. All samples were fractured at liquid nitrogen temperature. All micrographs were taken in COMPO mode in order to differentiate between polymer and filler. Finally, all samples were additionally examined through an EDAX attachment for a quantitative surface chemical analysis.

3. Results and Discussion

3.1. Flame Resistance and Tensile Properties. Table 2 presents the results of flame resistance and tensile properties of the compositions presented in Table 1.

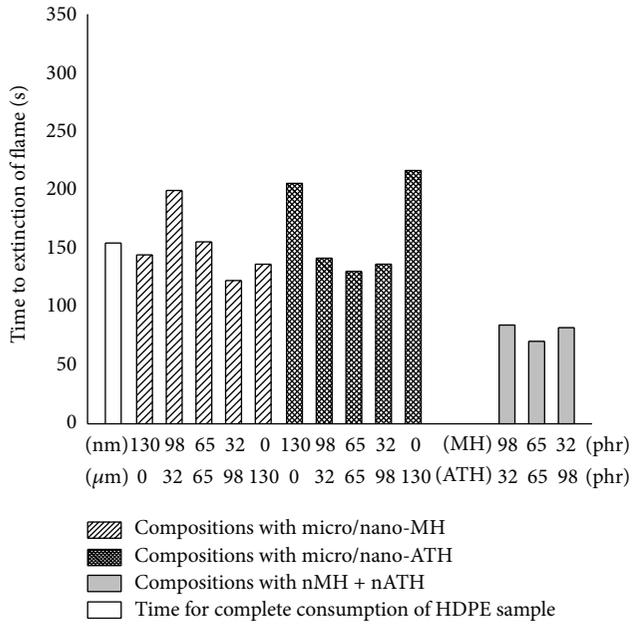


FIGURE 1: Time to self-extinction of flame during the UL-94-HB test of the compositions presented in Table 1. Note that all compositions contain 130 phr of flame retardant filler.

With respect to flame resistance, it can be observed that all compositions passed the UL-94-HB standard as autoextinguishable (AE), whereas only the MA3 (*with 65 phr nano-MH + 65 phr nano-ATH*) passed the UL-94-V as V1; all others failed, showing slight to intense dripping. The HDPE sample was rapidly consumed completely.

In this sense, we believe that the nanohydroxides create a network throughout the polymer matrix that slows down the free pass of oxygen in smaller areas, by creating micro- and nanolabyrinths, retarding as a consequence the process of combustion.

In order to differentiate between the UL-94-HB results, where all compositions were classified as AE, the time to self-extinction of flame was determined and the results are presented in Figure 1. It is observed that the times for the flame to extinguish itself varied from ca. 75 ± 5 s for the compositions with a mix of nano-MH and nano-ATH (MA2, MA3, and MA4) to ca. 135 ± 5 s for the compositions with a mix of micro- and nano-ATH (A2, A3, and A4), as well as for the compositions with a mix of micro- and nano-MH (M2, M3, and M4). Nevertheless, in none of these cases the flame advanced more than 3 cm.

According to this, the compositions with the better flame resistance should be those that self-extinguish sooner, that is, the compositions with a combination of nano-MH and nano-ATH, followed by the compositions with a combination of micro- and nano-ATH or a combination of micro- and nano-MH. The one which self-extinguished in the shortest time was the one with 65 phr nano-MH/65 phr nano-ATH (MA3), which is also the only one that was classified as V1 in the UL-94-V test. With respect to tensile properties, the compositions

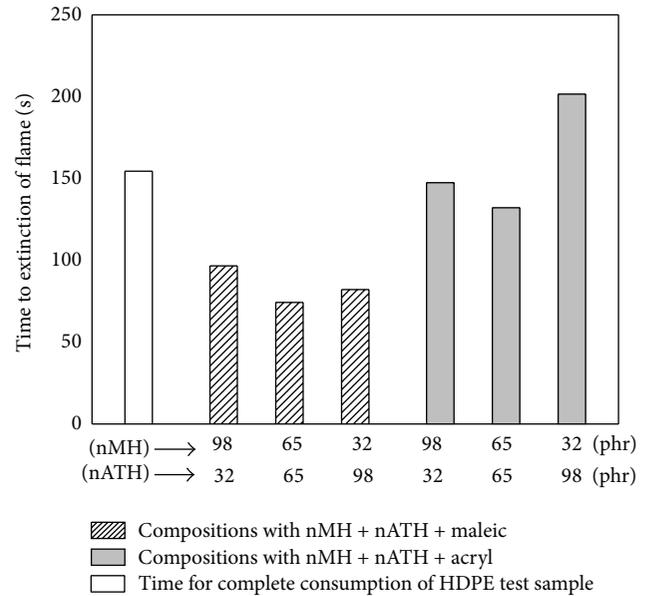


FIGURE 2: Time to self-extinction of flame during the UL-94-HB test of the compositions with compatibilizer, presented in Table 3.

TABLE 3: Compositions studied (continuation) (*all amounts are in phr*).

Compositions ^a	HDPE	EPDM	PEgMA	EMA	MH ATH	
					nm	nm
MA2maleic	80	10	10	—	98	32
MA3maleic	80	10	10	—	65	65
MA4maleic	80	10	10	—	32	98
MA2acryl	80	10	—	10	98	32
MA3acryl	80	10	—	10	65	65
MA4acryl	80	10	—	10	32	98

^a All compositions contain 0.2 phr silicon lubricant plus 0.15 phr antioxidant. MA compositions with a mix of nano-MH and nano-ATH, with compatibilizer.

with micro- and nano-MH and the compositions with nano-MH and nano-ATH present an average tensile stress (TS) of 14.7 and 14.4 MPa, respectively, which are in the same range of that of HDPE, whereas the compositions with micro- and nano-ATH present a lower average TS of 12.1 MPa. The elongation of all compositions, on the other hand, resulted much lower than that of HDPE. These results were attributed to the poor compatibility between polymer and filler, which was exacerbated by the high amount of filler.

Considering the above-mentioned results, two different compatibilizers (*maleic anhydride grafted polyethylene (PEgMA)* and *methyl acrylate grafted polyethylene (EMA)*) were added into compositions with a mix of nano-MH and nano-ATH (MA2, MA3, and MA4); the ones with the better flame resistance, substituting 10 phr of HDPE with 10 phr of compatibilizer, and the resulting compositions were analyzed. These are shown in Table 3. Figure 2 shows the time

TABLE 4: Flame resistance and tensile properties of compositions presented in Table 3.

Formulations	Flame resistance		Stress [MPa]	Tensile properties	
	UL-94-V	UL-94-HB		Elongation [%]	Modulus [MPa]
HDPE	Fails, drips	fails	16.0 ± 1.0	500 ± 40	340 ± 35
MA2maleic	Fails, drips	AE	20.5 ± 1.6	200 ± 15	440 ± 40
MA3maleic	V0	AE	20.7 ± 1.6	190 ± 10	430 ± 35
MA4maleic	Fails, drips	AE	19.9 ± 2.0	200 ± 20	445 ± 35
MA2acryl	Fails, drips	AE	16.3 ± 1.5	150 ± 15	450 ± 45
MA3acryl	V2	AE	16.7 ± 1.2	150 ± 10	440 ± 45
MA4acryl	Fails, drips	AE	15.8 ± 1.5	160 ± 15	440 ± 40

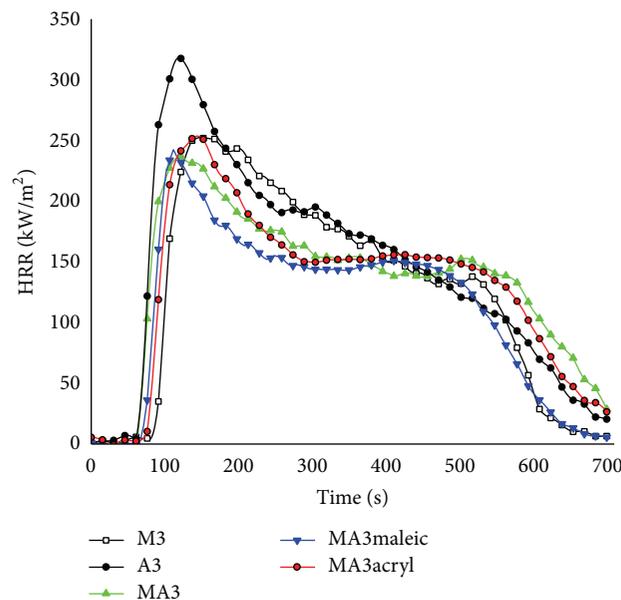


FIGURE 3: Heat release rate of compositions with 65 phr micro- and 65 phr nano-MH and 65 phr micro- and 65 phr nano-ATH (*M3* and *A3* from Table 1), as well as compositions with 65 phr nano-MH/65 phr nano-ATH, without and with compatibilizer (*MA3* from Table 1 and *MA3maleic* and *MA3acryl* from Table 3, resp.).

to self-extinction of flame during the UL-94-HB test of the compositions with compatibilizer, presented in Table 3.

Table 4 presents the flame resistance and tensile properties of the compositions with maleic or acrylate compatibilizer. Again, it can be observed that all six compositions passed the UL-94-HB standard as autoextinguishable (AE), and only the MA3maleic and the MA3acryl (with 65 phr nano-MH/65 phr nano-ATH each), plus PEGMA or plus EMA, respectively, passed the UL-94-V as V0 and V2, respectively. All others failed, showing slight dripping. The tensile stress showed clearly the effect of compatibilizer, especially those with PEGMA, which reached an average TS of 20.4 MPa. The elongation of all six compatibilized compositions, on the other hand, resulted much higher than without compatibilizer ($\sim 200\%$ when using maleic compatibilizer and $\sim 150\%$ when using acrylate compatibilizer), though still lower than that of pure HDPE.

First, the existence of van der Waals interactions between the HDPE and the PE of the PEGMA renders this blend of polyethylene and modified polyethylene compatible.

Additionally, the hydroxyl groups of the metallic hydroxides interact with the carbonyl groups of either the maleic anhydride or the methyl acrylate, via hydrogen bonding, increasing the compatibility between polymer and filler (Figure 4).

The heat release rate (HRR) is a measure of the rate of heat released to the surroundings per unit surface area of the burning material. Peak of heat release rate (PHRR) is the point of the highest rate of heat release. The higher the PHRR, the more likely the flame will self-propagate on the sample. The time to ignition is the time it took the sample to ignite after the test started. The time to PHRR is the time it took the sample to reach the PHRR. The total heat released (THR) is the total heat released since the time of ignition up to the time of flameout.

Heat release rate (HRR) has been found to be one of the most important parameters for evaluating material combustion and fire safety [15, 16].

Figure 3 shows the variation of HRR with time for HDPE as well as for the five selected compositions, as obtained from

TABLE 5: Data obtained from the cone calorimeter: time to ignition, time to reach the PHRR, heat release rate at the peak (PHRR), total heat released (THR) since ignition to flameout, and time to flameout.

	Time to ignition [s]	Time to peak HRR [s]	Peak HRR [(kJ/s)/m ²]	THR [MJ/m ²]	Time to flameout [s]
HDPE	63	150	2030.11	110.58	178
M3	86	155	255.35	86.71	593
A3	65	125	257.75	93.64	710
MA3	67	120	265.29	99.91	709
MA3maleic	76	125	240.44	79.61	597
MA3acryl	80	125	256.63	87.53	681

Note: 1 W = 1 J/s.

Data for HDPE was also obtained experimentally, though it is not shown in Figure 3.

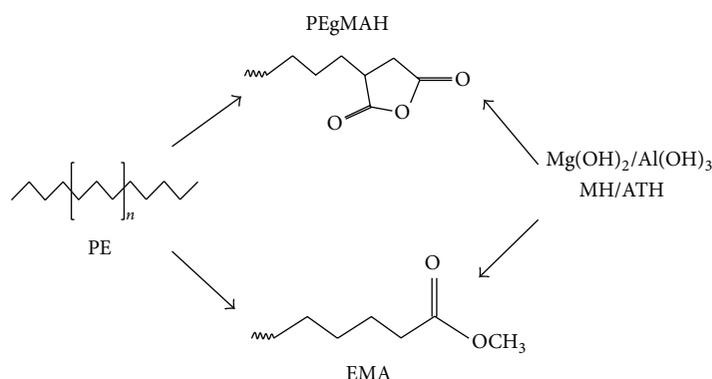


FIGURE 4: Hydrogen bond interactions between the hydroxyl groups of the metallic hydroxides and the carbonyl groups of either the maleic anhydride or the methyl acrylate.

the cone calorimeter analysis, and Table 5 shows the data obtained from the cone calorimeter, such as time to ignition, time to reach the PHRR, maximum HRR, and total heat released (THR) during the experiment, for HDPE as well as for the five selected flame resistant compositions examined.

First, it is observed that the HRR at the peak of the flame resistant compositions is ca. 8 times less than that of pure HDPE. Moreover, the time to flameout of pure HDPE is around 3.5–4.0 times less than that of the flame resistant compositions; that is, PE releases a great amount of heat (110 MJ/m²) in a very short period of time (178 s).

Second, though smaller, there is still a noticeable difference among the flame resistance compositions. The best all-around being the one designated as MA3maleic, with 65 phr nano-MH/65 phr nano-ATH, with PEGMA as compatibilizer (lowest PHRR and lowest THR).

This can be assumed to be due to the nanometric size of the flame retardant fillers and also due to the increased compatibility between polymer and filler, brought about by the PEGMA [10].

These results, which point to the MA3maleic as the best among the studied compositions, coincide with those obtained above with the UL-94-HB and UL-94-V tests.

3.2. Thermogravimetric Analysis (TGA). Figure 5 shows the TGA thermograms of MH, ATH, HDPE and the compositions with 65 phr nano-MH/65 phr nano-ATH, without compatibilizer (MA3) and with compatibilizer (MA3maleic and MA3acryl), which were the only ones that passed the UL-94-V.

First, it can be observed that the MH presents a weight loss of ca. 28 wt% between 350 and 440°C due to decomposition and liberation of water vapor, leaving approximately 72 wt% of magnesium oxide as residue. ATH presents a weight loss of ca. 34 wt% between 230 and 320°C due also to decomposition and liberation of water vapor, leaving approximately 66 wt% of aluminum oxide as residue.

Pure HDPE, on the other hand, decomposes and volatilizes between 380 and 490°C, leaving almost no residue.

It is important to point out that, according to the TGA results, the metallic hydroxides remained intact during processing, since the TGA thermograms of the prepared compositions coincide with the TGA thermograms of the individual fillers.

In the case of the 65 phr MH/65 phr ATH nanocomposites, without compatibilizer and with PEGMA and EMA compatibilizer (MA3, MA3maleic, and MA3acryl), they present

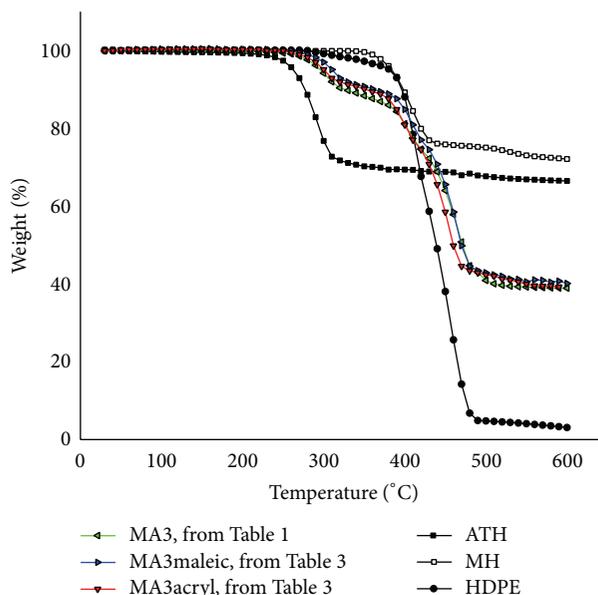


FIGURE 5: TGA thermograms of the MH and ATH hydroxides, HDPE and the compositions with 65 phr nMH/65 phr nATH, without and with compatibilizer (MA3 from Table 1 and MA3maleic and MA3acryl from Table 3).

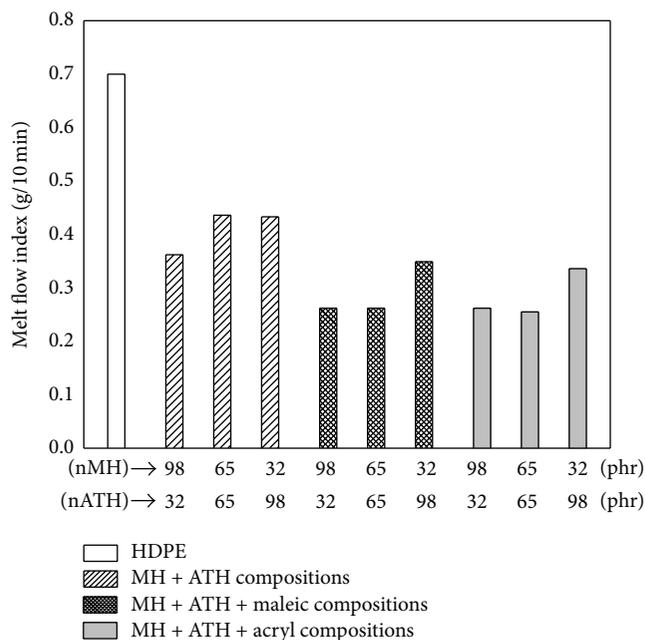


FIGURE 6: MFI of the 65 phr nano-MH/65 phr nano-ATH containing compositions, without compatibilizing agent and with maleic anhydride and methyl acrylate modified polyethylenes as compatibilizer.

very similar curves which superimpose each other. The three nanocomposites present the signals due to decomposition of ATH and liberation of water vapor between 280 and 320°C, and thereafter, due to decomposition of MH and liberation of water vapor between 380 and 420°C. Finally, the nanocomposites show another weight loss between 400 and 490°C due to the decomposition and volatilization of polyethylene and modified polyethylene, leaving approximately 38 wt% of aluminum and magnesium oxides as residue.

3.3. Melt Flow Index. Figure 6 presents the melt flow index of the nanometric Mg and Al hydroxide containing compositions, without compatibilizer and with maleic anhydride and methyl acrylate modified PE as compatibilizers.

First, as compared to that of pure HDPE, the MFI decreases with the addition of the metallic hydroxide fillers, as should have been expected. Second, comparing the compositions with metallic hydroxides, it is observed that (a) the MFI of the compositions with compatibilizer appears negligibly

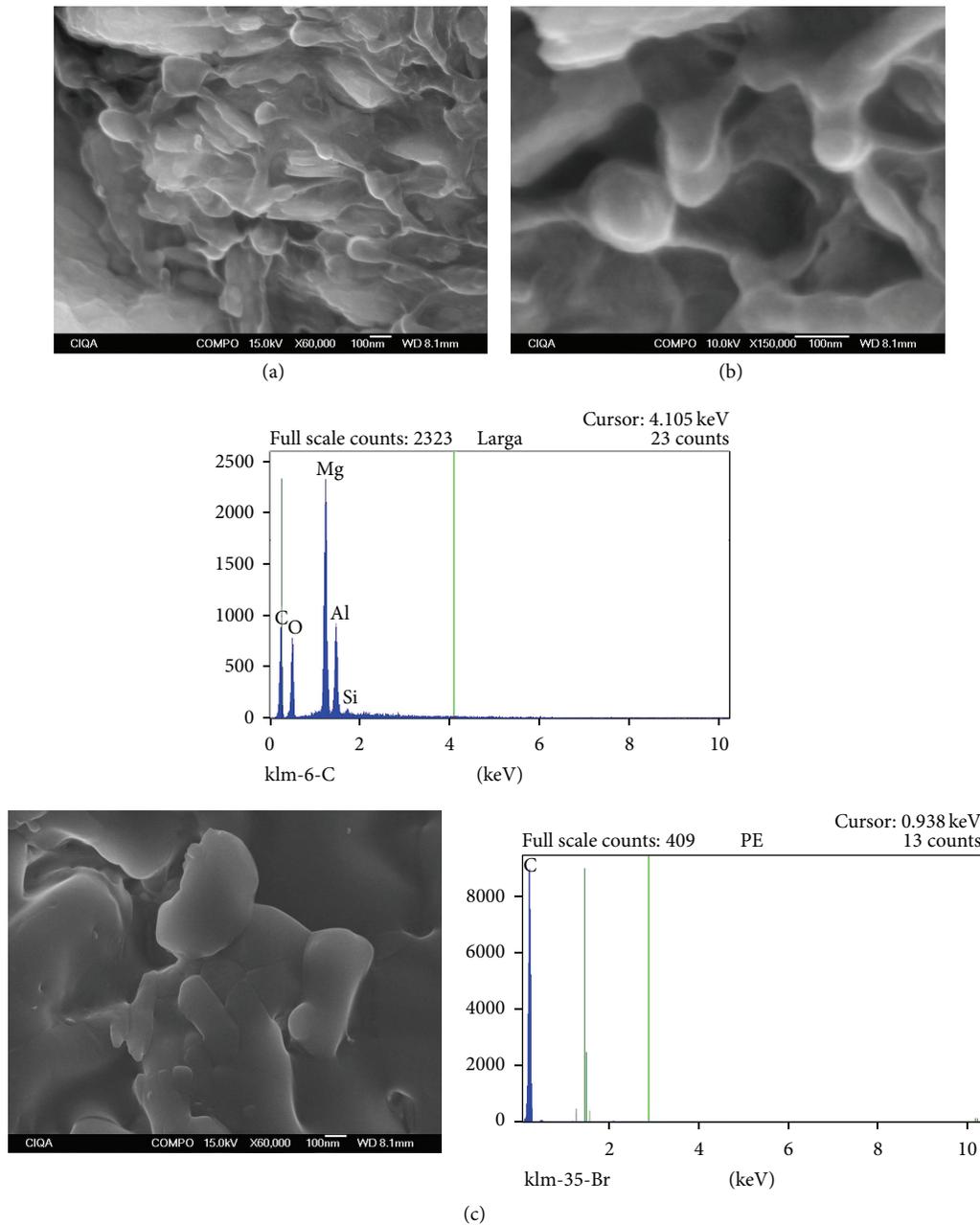


FIGURE 7: STEM micrographs of the 65 phr nano-MH/65 phr nano-ATH composite, without compatibilizer (MA3), at (a) 60,000x and (b) 150,000x, with their corresponding EDAX quantitative chemical analysis, as well as a micrograph of pure polyethylene (c), at 60,000x, with their corresponding chemical analysis.

lower and (b) there is no difference with respect to the effect of the two different compatibilizers.

3.4. Morphological Characterization. Figures 7(a) and 7(b) show STEM micrographs of the 65 phr MH/65 phr ATH nanocomposite, without compatibilizer (Figures 7(a) and 7(b); sample MA3), where agglomerates of filler particles are observed, which surely contributed to the very low tensile elongation; nonetheless, this morphology was sufficient for the MA3 composition to pass the UL-94-V test as V1.

In addition, Figure 7(c) shows a STEM micrograph of the pure polyethylene, where very smooth zones, without filler, are observed. Figures 7(a) and 7(b) present an EDAX chemical analysis showing the presence of both magnesium and aluminum hydroxides, whereas Figure 7(c) presents an EDAX analysis showing only the presence of carbon.

Figures 8(a) and 8(b) show STEM micrographs of the 65 phr nano-MH/65 phr nano-ATH composite, with PEGMA as compatibilizer (sample MA3maleic), where some particle agglomerates are still observed. However, in comparison

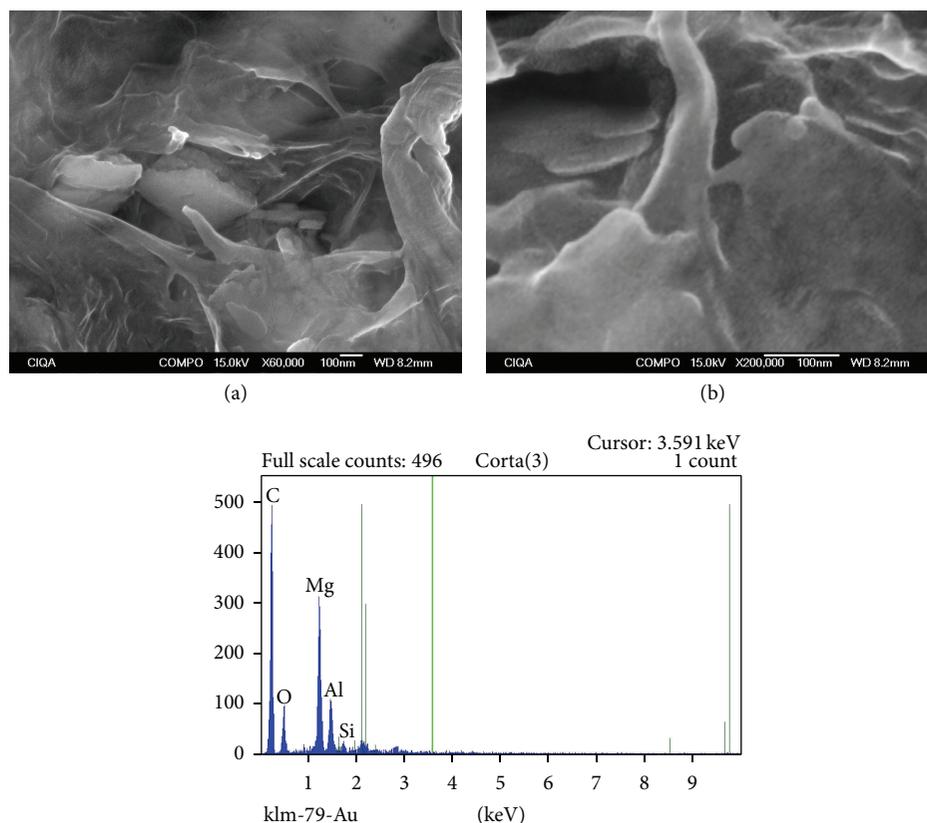


FIGURE 8: STEM micrographs of the MA3maleic composition, at (a) 60,000x and (b) 200,000x, with their corresponding EDAX quantitative chemical analysis.

with the similar composition, without compatibilizer (sample MA3), the filler particles now appear completely wetted by the polymer, surely due to the effect of compatibilizer. This effect contributed to a markedly greater TS and a slightly greater elongation of the MA3maleic composition. In addition, this MA3maleic passed the UL-94-V test as V0. An EDAX chemical analysis showed the presence of both magnesium and aluminum metallic hydroxides.

Figures 9(a) and 9(b) show STEM micrographs of the 65 phr nano-MH/65 phr nano-ATH composite, with EMA as compatibilizer (sample MA3acryl). Again, some agglomerates of filler particles are still observed. However, the filler particles appear completely wetted by the polymer. The presence of agglomerates, however, appears slightly greater when using this acrylate compatibilizer than when using the maleic compatibilizer.

The greatest TS (ca. 20 MPa) with moderate elongations (ca. 200%) were achieved with the composites with 65 phr nano-MH/65 phr nano-ATH, with PEgMA as compatibilizer.

An EDAX chemical analysis showed the presence of both magnesium and aluminum hydroxides. The EDAX elemental analysis showed that when the analysis is directed to the dispersed nanometric particles, the concentration of magnesium appears markedly superior to that of aluminum. On the contrary, when the analysis is directed towards the agglomerates, the concentration of aluminum is superior.

This leads to the assumption that, under these conditions, the ATH nanoparticles have a greater tendency to agglomerate than the MH nanoparticles.

4. Conclusions

All compositions studied throughout this work passed the UL-94-HB. All showed to be autoextinguishable, though the time to the self-extinction of flame varied.

The best compositions were those with a mix of nanometric magnesium and aluminum hydroxide. In addition, the composition with 65 phr nMH + 65 phr nATH (MA3) was the only one that passed the UL-94-V as V1. Nonetheless, the tensile properties of all these highly filled compositions were very poor, especially the elongation.

When adding a compatibilizer, maleic anhydride or methyl acrylate modified polyethylene, these compositions again passed the UL-94-HB. Moreover, these compositions (with 65 phr nMH + 65 phr nATH, with PEgMA or EMA) passed the UL-94-V as V0 and V2, respectively. But more noticeable, the effect of compatibilizer showed up in the tensile properties. The compositions with PEgMA reached an average tensile stress of 20.4 MPa, higher than that of pure HDPE, and an average elongation of 200%, lower than that of pure HDPE, but markedly higher than the compositions without compatibilizer.

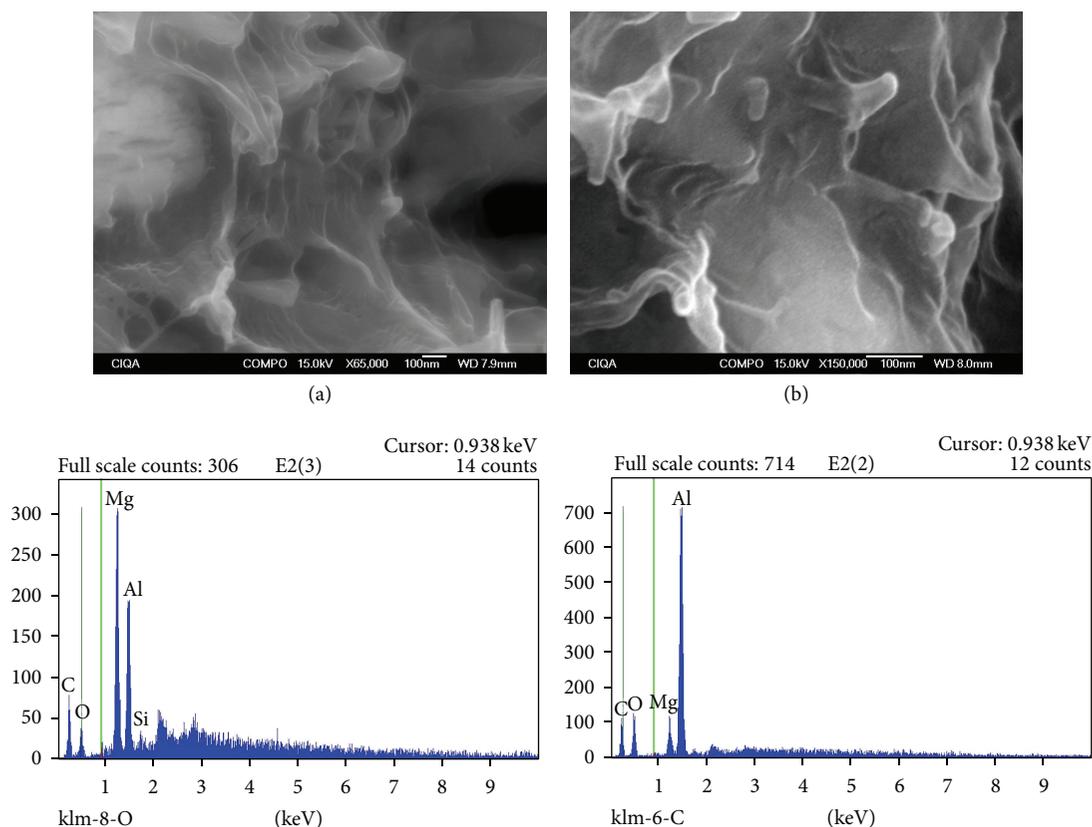


FIGURE 9: STEM micrographs of the MA3acryl composition, at (a) 65,000x and (b) 150,000x, with their corresponding EDAX quantitative chemical analysis.

Corroborating the results presented above, the cone calorimeter tests results showed the composition with 65 phr nMH + 65 phr nATH, with PEGMA as compatibilizer, to be the best among the studied compositions, with the lowest peak of HRR and THR.

Via STEM, it was observed that noncompatibilized samples showed many agglomerates, whereas the compatibilized samples showed much less agglomerates and, additionally, the filler particles now appeared completely wetted by the polymer, surely due to the effect of compatibilizer, especially the maleic anhydride modified polyethylene.

Finally, a punctual EDAX analysis showed that the aluminum concentration was always higher on the agglomerates, leading to the conclusion that the ATH presents a higher tendency to agglomerate than the MH.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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