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Use of Surface - Modified Magnesium Hydroxide
for Low - Smoke Flame Retardant Thermoplastics Applications

Dr. Tong Chen and Dr. Alex Isarov

J. M. Huber Corporation
251 Gordon Street, Fairmount, GA 30139
tel: 706-337-3243

Abstract

Magnesium hydroxide is an effective flame retardant and smoke suppressant for use in low-smoke, fire retardant plastic compounds for a variety of applications. The addition level of magnesium hydroxide into a polymer system varies from low to high depending on end use fire requirements. To assure uniform and easy incorporation of magnesium hydroxide into the polymer for maximized compound performance is always a key consideration in designing and engineering the final compounds. This is often achieved via use of the surface-modified magnesium hydroxide, with the surface modification designed to deliver enhanced compound performance. This paper discusses the effect of surface modification of magnesium hydroxide particles on such performance as processing behavior, mechanical properties, and fire performance. Application results are shown of the surface modified magnesium hydroxide in wire and cable compounds to help illustrate how to effectively design the high-performance fire retardant compositions through use of the surface modification.

Introduction

Magnesium hydroxide or MDH is used as a functional additive to impart flame and smoke performance to many polymer compounds, particularly in non-halogen, low-smoke applications. MDH has a dual functionality of flame retardancy and smoke suppression when heated to its decomposition temperature of about 340°C. At this temperature, MDH gives off about 31% of bound water by weight of the MDH used.

This endothermic decomposition reduces the heat generated in a fire while the released water suppresses smoke and dilutes potential fuel supply. MgO formed as a result of the MDH decomposition acts as charring layer that helps insulate potential fuel from heat and oxygen. The relatively higher thermal stability for MDH makes it more desirable for use in polypropylene and other engineering thermoplastics which often require the compounding and processing temperatures well above 200°C.
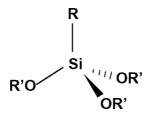
One concern with using MDH is its high loading levels (30-65% by weight) needed in order to meet the fire performance requirements, particularly for the polymers that are less inherently flame retardant. The higher MDH loading levels could result in reduced compound physical properties and cause concerns over material handling and dispersion quality during compounding. Therefore, assuring uniform incorporation of the MDH into the polymer is critical to achieving desired compounding processing and compound performance. By properly selecting polymer materials and using the surface-modified MDH suited for the given polymer system, one is able to reduce the difference in physical properties provided by MDH vs. the halogen-based flame retardants. Common considerations for choosing an MDH include the type of surface treatment and the level of the treatment for a given set of compound performance requirements.

Surface chemistry of MDH is determined by the presence of large amount of hydroxyl groups and some free moisture (0.1-0.3 % by weight). Unmodified MDH particles have hydrophilic surface thus less compatible with many non-polar or less polar polymers. This incompatibility between MDH and polymer often leads to poor dispersion and deterioration of physical properties of the compound including mechanical properties and flame retardancy. Chemical modification can change surface characteristics of the MDH particles, enabling particle functionalization by introducing the surface chemical groups that help couple the MDH to the polymer. Certain surface treatments also hydrophobize the MDH surface thus reducing moisture uptake.

Surface modification involves coating of a very thin layer of a certain chemical on the surface of MDH to impart a functionalized surface. There are three major categories of surface treatment chemicals:

1. Non Reactive, such as surfactants;

2. Reactive but non coupling, such as fatty acids and their salts, alkyl or phenyl silanes;

3. Reactive coupling, such as silanes containing vinyl, amino, sulfur, epoxy, or methacryl functional groups.

Fatty acids and silane coupling agents are most widely used chemicals for surface modification of MDH. A typical functional silane can be represented with a general structure shown below,

R
|
Si
R'O   ''''OR'
        OR'

where R represents the functional group that interacts or reacts with the organic material, such as polymers, while R' represents the functional group that reacts with inorganic material such as MDH.

Interaction between a functional silane and MDH surface can be described as shown in Figure 1.
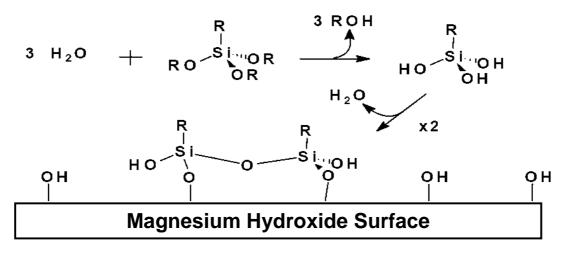
$$3\ H_2O \ + \ RO-Si(R)(OR)OR \ \longrightarrow \ 3\ ROH \ + \ HO-Si(R)(OH)OH$$

$$H_2O \quad \times 2$$

(siloxane oligomer grafted onto Magnesium Hydroxide Surface)

Magnesium Hydroxide Surface

Fig. 1. General mechanism of interaction between silane and MDH

The silicon-functional side of the silane molecule undergoes hydrolysis on MDH surface in the presence of surface hydroxyl groups and adsorbed moisture. Hydrolyzed silane molecules form hydrogen bond with the surface of mineral and/or undergo condensation reactions resulting in siloxane oligomers. Condensation reactions with surface hydroxyls are also possible leading to grafting of siloxane oligomers to the surface.

The organic-functional end of the silane molecule dictates how surface treated MDH interacts with the polymer. Non-coupling silanes improve wetting of the treated inorganic surface with the resin and the quality of dispersion. Coupling silanes may form a chemical bonding with the polymer thus significantly improve physical properties of the MDH-filled compounds.

Results and Discussion

Materials and Testing

Magnesium hydroxide: Vertex™ 100 made by J. M. Huber Corporation was used in this study. Vertex 100 has an average particle size (d_{50}) of about 0.8 microns, and a surface area of about 14 M^2/g.

Surface modification of MDH: Vertex 100 was treated with selected chemicals in a laboratory scale Henschel mixer under controlled conditions. The chemical modification was done in such a way that treated particles were free of agglomeration. Table 1 lists differently modified MDH used in this study.

Test compounds: Two polyolefin compounds and one PVC compound were used which were representative of commercial compounds used for wire and cable applications. One polyolefin compound is EVA with 28% VA content and contains 65% of MDH, another is impact polypropylene containing 55% of MDH. The PVC compound contains 28% of MDH in a K70 type resin with plasticizers. Other performance additives were also used in these compounds to represent commercial applications. All compounds were prepared in a Brabender mixer followed by two-roll milling of the mixture. All tests were performed according to ASTM and UL procedures, including sample preparation.

Table 1. Treated magnesium hydroxide used

Material	Surface modification
MDH-1	None
MDH-2	Aminosilane
MDH-3	Vinylsilane
MDH-4	Non-coupling silane
MDH-5	Fatty acid
MDH-6	Polymeric
MDH-7	Organo-phosphate

Fire performance

Table 2 shows results of several fire testing for different compounds. UL-94 was performed on 1/16" thickness plaques. Cone calorimetry tests were done per ASTM E1354 on plaques of 0.125" thickness using 50kW/M^2. For the EVA compound as shown in Table 2a, MDH modified with aminosilane (MDH-2) and vinylsilane (MDH-3) show improved overall fire performance vs. unmodified MDH (MDH-1) and fatty-acid

modified (MDH-5). While all four compounds in Table 2a passed UL 94 V0, MDH-2 and MDH-3 showed improvements in heat and smoke reduction, as well as improved flammability indicated by increased LOI values (limiting oxygen index). Both aminosilane and vinylsilane used in modifying surface of MDH-2 and MDH-3 provided effective coupling between MDH and EVA.

Table 2a. Effect of MDH surface modification on fire performance for EVA-based compound

Material →	MDH-1	MDH-2	MDH-3	MDH-5
LOI, %	38	40	40	38
UL-94	V-0	V-0	V-0	V-0
Time to Ignition, s	75.81	73.58	71.10	75.01
Peak RHR, kW/m^2	236.17	204.65	211.4	309.95
Time of Peak RHR, s	71.67	36.3	72.93	73.1
Average SEA, m^2/kg	303.01	268.99	156.62	296.37
Time of Peak SEA, s	455	570	723.33	365

Figures 2a and 2b show actual heat release and smoke development profiles, respectively, for the four MDH materials listed in Table 2a. The more effective retarding and suppression of compound flame and smoke with MDH-2 and MDH-3 are evident. For the EVA compound system used, modifying MDH surface with aminosilane or vinylsilane prior to compounding into the polymer can markedly benefit the fire performance.
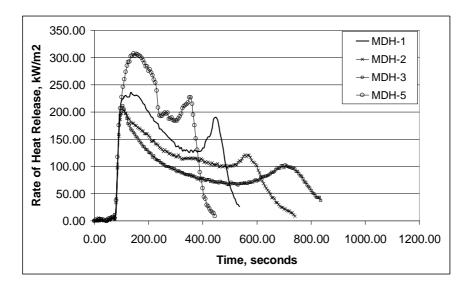

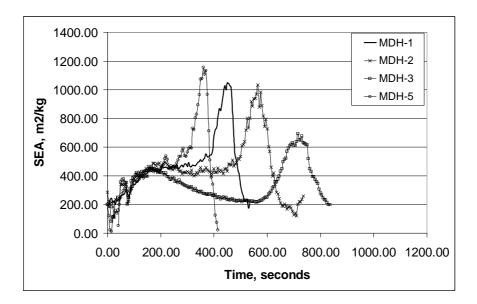**Fig. 2a. Cone calorimetry heat release for MDH-filled EVA compound**

Fig. 2b. Cone calorimetry smoke generation for MDH-filled EVA compound

While surface-modifying the MDH enhances the fire performance as noted early for highly filled EVA system, such benefit can be reduced when MDH loading levels are lower. For flame retardant PVC compound applications, since PVC is inherently more flame retardant than other polymers like EVA, use of externally added fire retardants is relatively lower. In such cases, whether the surface-modified MDH can bring added performance benefit needs to be scrutinized.

Table 2b shows compound fire performance for a flexible PVC compound with about 28% of MDH loading level, comparing an alkoxysilane-treated MDH (MDH-4) with an untreated MDH (MDH-1). In addition to the cone calorimetry test, we also evaluated the material smoke property using an NBS smoke chamber, tested in both non-flaming and flaming mode.

It is interesting to note that, while non-coupling silane can improve dispersion of MDH in a PVC resin, our testing shows that pre-treating MDH with such a silane did not enhance the overall fire performance to the extent noted in the MDH-filled EVA compounds. For many plasticized PVC systems where one or more plasticizers are present at high levels, care must be taken when using surface-treated MDH to assure that the MDH undergoes desirable coupling with the resin rather than with the plasticizers.

Table 2b. Comparison of treated vs. untreated MDH in a PVC compound

Material →	MDH-1	MDH-4
LOI (%)	38-39	38-39
UL 94 Vertical ($\frac{1}{16}$")	V-0	V-0
NBS E622 Smoke: Non-Flaming		
Dm @ 4 min.	27.33	41
Dmax	271.67	268.67
NBS E622 Smoke: Flaming		
Dm @ 4 min.	49.33	62
Dmax	469.67	386.33
Cone Calorimetry:		
Time to Ignition (s)	24.697	20.038
Peak RHR (KW/m2)	126.03	138.57
Time of Peak RHR (s)	193.33	186.67
Total Heat Released (MJ/m2)	35.07	38.97
Avg. Eff Heat of Comb. (MJ/kg)	12.81	12.65
Avg. SEA (m2/kg)	538.48	526.84
Time of Peak SEA (s)	50.00	40.00

Mechanical properties

As mentioned in the introduction, addition of metal hydroxide flame retardant such as MDH into a polymer typically reduces the mechanical properties of the compounds as compared to some halogen-based flame retardants. The challenge then becomes as to how to find a way to achieve the best balance among key properties and performance.

Results for several physical properties are given in Table 3a for the EVA compound, and in Table 3b for the polypropylene compound.

Table 3a. Effect of MDH modification on physical properties – EVA compounds

Material →	MDH-1	MDH-2	MDH-3	MDH-5
Tensile Strength, psi	1610	1962	1486	1398
Elongation at Break, %	108	134	128	51
Brittleness Temperature, deg C	-9.5	-14	-9	2

For the EVA, it is clear that MDH-2 provided the best mechanical property combination, while MDH-3 essentially retained the performance of the untreated MDH. Referring back to the data shown in Table 2a, MDH-3 had the best flame and smoke performance. Therefore, choice of the type of surface modification for MDH depends on the overall performance requirement considerations. Performance tradeoffs are commonly expected for these highly-filled flame retardant compounds from an application standpoint, but using a properly treated MDH can minimize such tradeoffs.

For polypropylene compound mechanical properties as given in Table 3b, there is also an issue of balancing the overall physical property. MDH-2 with an aminosilane surface modification gave best tensile strength but low in impact strength, while MDH-6 with a polymeric surface modification gave best impact property but lowest in tensile. MDH-3 with the vinylsilane treatment resulted in best color but intermediate in mechanical performance. MDH-5 had a good balance between tensile and toughness, but poor in color which could cause concern to the color-sensitive applications.

Table 3b. Effect of MDH modification on physical properties – PP compounds

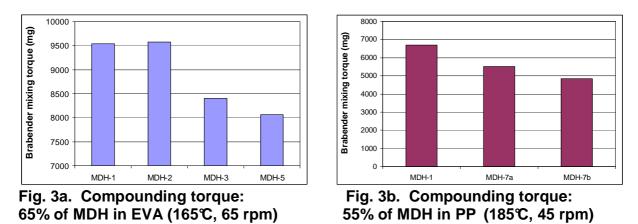| Material →	MDH-2	MDH-3	MDH-5	MDH-6
Tensile Strength, psi	3004	2699	2752	2087
Izod Impact strength, j/m	2.4	2.8	2.8	6.4
Color by yellowness index	20	13	40	20

Again, the choice of the type of surface modification will have to be based on the actual compound performance requirement for the given application. For color-insensitive applications, MDH-5 can be a good choice based on cost-performance balance. For the applications requiring excellent material toughness, MDH-6 represents a preferred flame retardant additive.

Compounding rheology

Depending on the polymer used, addition of MDH into the polymer can pose challenges to compounding processing due to changes in the material rheology, both with batch and continuous mixing processes. While use of the easy-processing polymers can help mitigate such processing issues, use of the properly surface-modified MDH can also, sometimes significantly, improve the processing rheology, thus maximizing the compounding throughput while reducing energy cost.

Figure 3 shows the effect of MDH surface modification on achieving more favorable processing characteristics of the MDH-filled polymer systems, 3a for the EVA and 3b for PP, respectively. MDH-7a and -7b shown in Figure 3b were treated with the same

organo phosphate but at different treatment levels, with 7b treated at twice the level of 7a.

Fig. 3a. Compounding torque: 65% of MDH in EVA (165°C, 65 rpm)

Fig. 3b. Compounding torque: 55% of MDH in PP (185°C, 45 rpm)

It is clear from the Figures 3 above that there are processing benefits achievable via use of the properly treated MDH for a given polymer system. We noted earlier that MDH-5 with a fatty acid treatment was not as effective as other silane treatments in affecting the fire performance and mechanical properties. However, as shown in Figure 3a, the fatty acid treatment is particularly effective in improving processing rheology thus maximizing the compounding throughput. In Figure 3b, we investigated two level of the same organo-phosphate treatment on MDH, and found an improvement in processing rheology over the untreated MDH, such an improvement increased with increasing level of surface treatment.

Clearly, the processing rheology consideration is only one of many elements of the MDH-filled compound engineering, and its optimization needs to be balanced against other performance considerations particularly the fire performance. It is worth pointing out that our earlier studies also conclude that excessive surface treatment of the MDH, while perhaps benefiting the processing, can invariably lead to significant reduction in other fire, mechanical and electrical properties and performance.

Conclusions

A number of different chemical treatments were investigated for use in modifying the surface characteristics of a magnesium hydroxide material, Vertex 100 made by J. M. Huber Corporation, in order to compare the effect of various surface modifications on the compound performance. Three flame retardant polymer compound systems were examined, EVA, polypropylene and PVC. The study shows that aminosilane- and vinylsilane-treated MDH benefit the fire performance of the EVA, particularly for highly MDH-filled compounds. Fatty-acid treated MDH can enhance compounding processing although it could reduce the physical and mechanical properties especially with overly treated MDH. For the PP studies, it is found that certain surface treatments can

beneficiate one mechanical property more than with the others, for example, tensile strength over impact strength. Choice of a specific surface treatment needs to depend on the actual performance requirement such that the overall performance is optimized. For the PVC compound studied with a lower MDH loading level, a non-coupling silane treated MDH did not seem to provide much performance benefits vs. the untreated MDH control. This illustrates that care needs to be taken when dealing with the lowly filled MDH compound systems to determine a suitable MDH in order to assure desirable cost-performance balance in compound engineering.

In summary, this study also shows that there tend to tradeoffs in compound performance and properties with any surface treatment for MDH for a polymer application. Therefore, one needs to be diligent in choosing the right surface treatment that assures maximization of the desirable property and performance while keeping the tradeoffs at acceptable levels.

Author contact information:
    Tong Chen: 706-337-3243, ext 4106; tchen@huber.com
    Alex Isarov: 706-337-3243, ext 4116; aisarov@huber.com