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Magnesium hydroxide flame retardant and its application to a low-density polyethylene/ethylene vinyl acetate composite

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Magnesium hydroxide as a halogen-free flame retardant attracts increasing attention due to environmental regulations and its unique physical properties such as non-toxicity and smoke suppressant ability during combustion. Low-density polyethylene/ethylene vinyl acetate(LDPE/EVA) blends are one of the polyolefins of which the flame retardance is enhanced by compositions containing magnesium hydroxide. Natural magnesium hydroxide flame retardant is available from the mineral brucite by the adjusting size distribution and surface treatment. A synthetic magnesium hydroxide is usually prepared by precipitation and hydrothermal treatment from magnesium salts or hydrolysis of MgO mineral(periclase). Natural and synthetic magnesium hydroxide have been prepared and mixed with LDPE/EVA by melt compounding. The dependence of the particle size and purity of the magnesium hydroxide and various additives for the synergistic effect on the flame retardance of LDPE/EVA has been studied through combustion tests of the polymer composites. The combustion behavior has been tested by limited oxygen index tests and the vertical burning tests of UL-94.

Key words: Magnesium hydroxide, Flame retardant, LDPE/EVA, Composite, LOI, UL-94.

Introduction

Environmental regulation are getting stronger to limit the use of halogen flame retardants and thereby alternative halogen flame retardants are in demand. Hydroxides, several organic/inorganic phosphrous compounds, and N-group compounds such as the melamine type may be classified as promising non-halogen flame retardants, of which magnesium hydroxide has attracted increased attention due to its non-toxicity, good processability(lower melt flow index and higher processing temperature due to higher decomposition temperature compared to aluminum hydroxide), and smoke suppressant ability during combustion [1]. However, it has been known that a high loading of magnesium hydroxide is a drawback so that there are many investigations on the incorporation of magnesium hydroxide with other additive agents for a synergistic effect [1, 2]. The additives to magnesium hydroxide flame retardants such as silica [2], zinc hydroxystannate [3], zinc borate [4, 5], graphite[6], red phosphorous[7], phosphorous compounds [1], or nitrate salts [1], etc were found to be effective with various types of polymers. However, magnesium hydroxide itself may vary in its flame retardant capability depending on its particle size, crystallinity, surface area, surface modification, and dispersion [1]. In the study of physical properties of magnesium hydroxide and their effect on a polypropylene composite, the dispersion is a key factor for the mechanical strength and flame retardance of the polymer composite. The BET surface area is also found to be highly correlated to the mechanical property and flame retardance so that a higher surface area (that is, a smaller particle size) results in a higher flame retardance (higher LOI) and higher mechanical strength but lower melt flow index (MFI) in the range of BET upto 15 m²/g at 60 wt% loading of magnesium hydroxide [1]. However, the correlation between physical and chemical properties of magnesium hydroxide and flame retardance is not clear in terms of some properties, such as the effect of chemical purity, loading, average particle size of magnesium hydroxide, and type of polymers.

Low-density polyethylene/ethylene vinyl acetate (LDPE/ EVA) blends are widely used in the cable industry as excellent insulating materials with good physical and mechanical properties. This is also one of the polyolefins where the flame retardance is enhanced by compositions containing magnesium hydroxide. Several magnesium hydroxides were compared in terms of their physical properties and flame retardance in this study. Natural magnesium hydroxide flame retardant is available from the mineral brucite by milling to a certain average particle size and distribution and given a surface treatment. A synthetic one is usually prepared by precipitation and a hydrothermal treatment from magnesium salts or hydrolysis of MgO mineral(periclase) [8]. Depending on the preparation

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method, the particle size and shape varies, nano to micro with plate, fibrous, spherical, and flower-like type shapes. However, there no systematic comparison of these particles has been made in terms of flame retardance when they were applied to a polymer composite. Magnesium hydroxide flame retardants have been applied to polypropylene(PP), ethylene vinyl acetate(EVA) [2, 9], and LDPE/EVA [10, 11] composites so that they are applied not only as a cable wire covering material but also in automobiles, home appliances, and building materials.

Natural and synthetic magnesium hydroxide has been prepared and mixed to LDPE/EVA composite by melt compounding. The dependence of the size and purity of the magnesium hydroxide and various additives a synergistic effect on the flame retardance of LDPE/EVA has been studied through combustion tests of the flame retardant (FR)-polymer composites.

Experimental Procedure

Commercially available Mg(OH)₂ flame retardants were collected for a comparison of their flame retardant characteristics toward FR-LDPE/EVA composites. Two natural Mg(OH)₂ with different average particle sizes, M3-C2 and M16(TAJIMA, Nanotech Ceramics Co. Ltd) and a synthetic one, K(KISMA-5A, Kyowa, Japan) were investigated.

Synthetic Mg(OH)₂ was also prepared from MgCl₂ by precipitation and a hydrothermal treatment in the laboratory and named KM-P and KM. 2 M magnesium hydroxide hydrate was mixed with 2 M NH₄OH or NaOH in a 1 : 2 molar ratio of Mg(OH)₂ and alkali and given a hydrothermal treatment at 180 °C for 20 h. The precipitates were washed with water and ethanol. The precipitates were re-dispersed in ethanol to be ~30 wt%. 2 wt% silane (Z-6341, Dow corning) was added to the precipitates and the slurry was stirred for 6 h so that the surface of the magnesium hydroxide particles may be coated with silane from hydrolysis and condensation. The precipitates after the hydrothermal is named KM and without the hydrothermal treatment named KM-P.

Mg(OH)₂ flame retardants were characterized by their chemical composition, average particle size and distribution, morphology, crystal structure, surface properties, and by thermo-gravimetric analysis. The chemical composition was analyzed by an ion coupled plasma optical emission spectrometer (ICP-OES), the size by a particle size analyzer (Mastersizer X, Malvern Instruments Ltd.), their morphology by a field emission scanning electron microscope(FE-SEM) (JSM 6700F, JEOL), the BET surface area by nitrogen adsorption(ASAP 2010, Micrometrics), their thermal properties by a thermo gravimetric-differential scanning calorimeter(TG-DSC, STA409C/3/F, Netzsch), and their the crystal structure by X-ray diffraction (XRD, MXP, Mac Science).

They were used for the preparation of FR-LDPE/EVA composites with 50, 55, and 60 wt% loading of flame

retardants. The synergistic effect of the additives, redphosphorous, phosphite ester(TAJIMA-NP, Nanotech Ceramics Co. Ltd), and a Si-compound(RM4-7081, Dow corning), were tested by 10% substitution of the additives for the flame retardants and the total FR loading was fixed to be 50 wt% in the FR-LDPE/EVA composite.

Low density polyethylene with an MFI lower than 5 was supplied by Hanwha Petrochecmial Corp. and poly (ethylene-co-vinyl acetate)(EVA) was the cable grade VS430 with 26% of vinyl acetate supplied by Honam Petrochemical Corporation. The polymer matrix used was a blend of LDPE and EVA in a ratio of 1 : 1. The flame retardant- filled composites were processed using a high viscosity kneader (Brabender mixer) at a speed of 60 rpm at 130 °C with a torque of 4-15 Nm for 10 minutes. After mixing, the samples were hot-pressed at 41 MPa(6,000 psi) to sheets of a suitable thickness and size for 5 minutes at 230 °C.

The composite samples were characterized mainly by their limited oxygen index(LOI) and combustion tests according to UL-94. The LOI corresponds to the minimum percentage of oxygen needed for the combustion of specimens measuring $120 \times 10 \times 4$ mm in an oxygennitrogen atmosphere in accordance with ISO 4589 standard. The UL-94 vertical burning tests were carried out using a UL94 AVH chamber(FESTEC International Co., LTD.) on sheets of $127 \times 12.7 \times 3$ mm according to the standard UL-94 test ASTM D635-77.

Results and Discussion

The physical properties of commercially-available $Mg(OH)_2$ flame retardants, M3, M16, K and the laboratory made KM and KM-P are compared in terms of chemical compositions (Table 1) and average particle size (Table 2). The purity of natural ones is lower than that of synthetic ones. The average particle size of natural ones is larger

Table 1. Chemical compositions of natural and synthetic $Mg(OH)_2$ flame retardants

Sample	Natural	Synt	thetic
	M16	К	KM*
Mg(OH) ₂	94	98.0	98.3
Ca(OH) ₂	2.22	0.04	0.19
Fe_2O_3	0.25	< 0.01	< 0.01
P_2O_5	0.05	< 0.01	< 0.01
SiO_2	< 0.01	0.06	< 0.01

* KM before surface treatment

Table 2. Average particle size(μm) of natural and synthetic $Mg(OH)_2$ flame retardants

Sample —	Nat	Natural		Synthetic		
	M3	M16	K	KM	KM-P	
D50	4.0	20	2.7	2.3	1.1	



Fig. 1. SEM morpholgies of natural and synthetic Mg(OH)₂: (a) M3, (b) M16, (c) K, and (d) KM.



Fig. 2. SEM morpholgies of Mg(OH)₂ with/without a hydrothermal treatment : (a) KM, (b)KM-P.

than that of the synthetic ones. However, the primary particle size of KM-P is 100-200 nm, so that the average particle size measured by a diffraction method may be considered as that of the secondary particles which are aggregated. According to morphologies seen by SEM(Figs. 1 and 2) the hexagonal plate shape is well developed and the aspect ratio is very large in synthetic ones compared to the natural ones, which are shaped by the milling. They do not show a clear crystallite shape, however, all clearly show strong x-ray diffraction patterns corresponding to the hexagonal structure (Fig. 3). The natural magnesium hydroxides are seen to be larger in particle size in SEM images. The laboratory made magnesium hydroxide after a hydrothermal treatment, KM, is much larger in particle size compared to the one with just precipitation without a hydrothermal treatment, KM-P. (Fig. 2) The BET surface area is 9.0 m²/g for KM and 51 m²/g for KM-P, so that we clearly see the distinctive difference in surface areas and particle sizes. The typical XRD powder pattern of samples were indexed as the hexagonal structure of Mg(OH)₂ with the lattice constants comparable to the values of JCPDS 7-239. The peaks arising from KM-P are significantly broad, which indicates that the Mg(OH)₂ particles have a very small grain size. Comparing the intensity ratio



Fig. 3. X-ray diffraction pattern of natural and synthetic $Mg(OH)_2$: (a) M3, (b) M16, (c) K, (d) KM, and (e) KM-P.

Table 3. X-ray diffraction intensity ratio of $I_{(001)}\,/\,I_{(110)}\, of$ natural and synthetic $Mg(OH)_2$

	I / I		
Mg(OH) ₂	Source	Code	$-\mathbf{I}_{(001)} / \mathbf{I}_{(110)}$
Natural	Commercial	M3	23.2
Natural	Commercial	M16	25.3
Synthetic	Commercial	Κ	7.9
Synthetic	Lab. made	KM	57.9
Synthetic	Lab. made	KM-P	2.2

Sample	LDPE	EVA	Mg(0	LOI	
	wt%	wt%	Туре	wt%	LOI
1	25	25	M3	50	27.7
2	22.5	22.5	M3	55	28.2
3	20	20	M3	60	30.9
4	25	25	M16	50	26.1
5	22.5	22.5	M16	55	27.7
6	20	20	M16	60	28.6
7	25	25	Κ	50	23.9
8	22.5	22.5	Κ	55	28.2
9	20	20	Κ	60	36.5
10	25	25	KM	50	29.2
11	22.5	22.5	KM	55	33.0
12	20	20	KM	60	37.7
13	25	25	KM-P	50	26.8
14	22.5	22.5	KM-P	55	31.6
15	20	20	KM-P	60	32.7

Table 4. Composite sample compositions and their LOI values

between reflections (001) and (110) gives a possible difference of particle shape (Table 3). The higher I_{001}/I_{101} ratio indicates a larger aspect ratio. For the commercially-available samples, natural ones show a higher ratio than the synthetic one but KM gives as high a ratio as the natural



Fig. 4. LOI values with an increase of flame retardant loadings for various flame retardants natural $Mg(OH)_2$: (a) M3 and (b) M16, and synthetic $Mg(OH)_2$: (c) K, and (d) KM, and (e) KM-P.

ones. Even though it is difficult to tell the difference of K and KM in their morphologies seen by SEM, KM has higher ratio of I_{001}/I_{101} , which means the aspect ratio of the hexagonal layer to its thickness is larger.

In the melt compounding process, the FR filled composite samples were relatively poor in processability needing a higher torque than the lower loading LDPE/EVA composites, but all were prepared relatively easily without any difference in outcome.

The compositions and LOI of FR-LDPE/EVA composite samples are listed in Table 4 and Fig. 4. The higher the loading of FR, the higher the LOI is without exception. The LOI of the composite with synthetic magnesium hydroxide is higher than that of natural ones at 60 wt% loading, however, at 50 wt% FR loading, the LOI of the composite filled with natural was smaller than that of commercial synthetic magnesium hydroxide even though its average particle size is larger and the $Mg(OH)_2$ purity is lower. The purity of Mg(OH)₂ might not be a key factor in determining flame retardancy. The size dependence shown here is that the smaller particles lead to higher LOI when we compare M3 and M16 as found in PP composites [1]. However, when we compare KM and KM-P, the particle size of KM-P is smaller but the LOI value is also smaller than that of KM. The size dependence may be explained only within a certain range of average particle size and when the particle shapes and size distributions are similar.

 Table 5. LDPE/EVA composite samples prepared with additives of red-P, P-ester, and a Si compound to magnesium hydroxide and their LOI values

Sample LDPE wt%	EVA wt%	Mg(OH) ₂		Additives		LOI	
		Туре	wt%	Туре	wt%	LOI	
1	25	25	KM	50	-	-	29.2
2	25	25	KM	45	Red-P	5	36.2
3	25	25	KM	45	P-ester	5	28.1
4	25	25	KM	45	Si-compound	5	36.1



Fig. 5. FR-LDPE/EVA composite samples after vertical burning test with 50, 55, and 60 wt% magnesium hydroxide loadings.

The reason for a lower LOI of KM-P than KM may be explained by its aggregation and an uneven distribution of FR in the composite.

Finally, the synergistic effect of additives was observed for red-phosphorous and a Si-compound but not for phosphite ester (Table 5). The former two are inorganic powder types but the latter was an organic liquid type so that they might not be miscible with the olefin compound with a lower thermal stability. With the synergistic additives, the loading of FR may be lowered to 50 wt% while keeping the LOI as high as the LOI of 60% loaded composite sample with a sole contribution of Mg(OH)₂.

The vertical burning tests of UL 94, 60 wt% FR-LDPE/ EVA composites were all graded V-0, but lower loaded samples were not satisfactory in both burning time and ignition of a cotton ball due to drips from the composite while burning (Fig. 5). It is noteworthy that the flame retardance of natural magnesium hydroxide is as good as the retardance of synthetic ones at 60% loading based on the UL-94 test. Even though the LOI value is not the highest for KM-P, the vertical burning test give the highest grade for the 55% loaded sample and the specimen hardly burnt at 60% loading specimen. This might be explained due to the dispersion of small particles even though there are aggregations, which makes the ignition time longer.

Conclusions

FR-LDPE/EVA composites were prepared with natural and synthetic magnesium hydroxide flame retardants. The purity of natural $Mg(OH)_2$ is lower than synthetic Mg(OH)₂ but it seems to be not a critical factor in changing the flame retardance since 50 wt% loaded FR-LDPE/EVA composites showed higher LOI and retained their original shape after the burning test. The average particle size contributes to the flame retardance. The smaller average size of particles is, the higher the LOI is but the small primary particles, as small as 100-200 nm, did show the lower LOI than the expected from the particle size. Therefore, a small particle distribution in the composite is very important to retain the flame retardance. From the UL-94 tests, smaller particles gave better flame retardance. There is some difference in flame retardance predicted from LOI and UL-94 combustion tests. 10% of additives to magnesium hydroxide FR revealed synergistic effect on LOI so that the loading of the FR may be lowered to 50 wt% while keeping an LOI as high as the LOI of 60% loaded composite sample with the sole contribution of Mg(OH)₂. Red-phosphrous and R4-7081 revealed a synergistic effect but a phosphite tested in this experiment did not.

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References

- 1. D. Koda, in "Scientific approach toward flame retarancy" (in Japanese) edited by K. Takeda (Japan Technology Association, 2004) p.262-266.
- 2. M. Fu and B. Gu, Polym. Degrad. Stab. 85 (2004) 633-639.
- 3. M.S. Cross, P.A. Cusack and P.R. Hornsby, Polym. Degrad. Stab. 79 (2003) 309-318.
- 4. G. Fontaine, S. Bourbigot, S. Duquesne, Polm. Degrad. Stab.

93[1] (2008) 68-76.

- 5. F. Carpentier, S. Bourbigot, M.L. Bras, R. Delobel and M. Foulon, Polym. Degrad. Stab. 69 (2000) 83-92.
- 6. Z. Li, B. Qu, Polym. Degrad. Stab. 81 (2001) 401-408.
- 7. M. Pecht. Y. Deng, Microelectronics Reliability 46 (2006) 53-62.
- H. Qian, M. Deng, S. Zhang and L. Xu, Materials Science and Engineering A, 445-446 (2006) 600-603.
- L. Qiu, R. Xie, P. Ding and B. Qu, Composite Structures 62 (2003) 391-395.
- L. Haurie, A.I. Fernanadez, J.I. Velasco, J.M. Chimenos, J.-M.L. Cuesta and F. Espiell, Polym. Degrad. Stab. 91 (2006) 989-994.
- L. Haurie, A.I. Fernanadez, J.I. Velasco, J.M. Chimenos, J.-M.L. Cuesta and F. Espiell, Polym. Degrad. Stab. 92 (2007) 1082-1087.