

Performance and decomposition behavior of hydromagnesite Mg (OH)₂ Synergistic polyethylene flame Retardant composites

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Abstract: The flame retardant polyethylene (PE) matrix composites were prepared by twin-screw extruder, with hydromagnesite (HM) and Mg(OH)₂ as the flame retardants. The flame retardant properties and mechanism of HM-Mg(OH)₂/PE flame retardant composites were investigated by limited oxygen index (LOI), Vertical burning Test (UL-94), Cone calorimetric Test (CCT) and universal tensile test. The thermal decomposition behavior of HM-Mg(OH)₂/PE flame Retardant Composites was studied by Thermogravimetric analysis (TGA). The results show that, the flame retardant in appropriate proportions of HM and Mg(OH)₂ decomposes in the combustion temperature range which leads to a better flame. In the premise of the same LOI and tensile strength, the cost of

PE Composite with synergistic flame retardant decreases significantly with Mg(OH)₂ as flame retardant alone. The ineffective even negative decomposition of HM reduces in the synergistic flame, and the inhibitory effect on the decomposition by the PE matrix with HM under high temperature is retained. At the same time, a

HeJunjie, CHENG Yu, ZHANG Xin, *et al* performance and decomposition behavior of HYDROMAGNESITE-MG(OH)₂ synergistic polyethylene flame retardant composites [J]. *Acta materiae Compositae sinica*, 2017, (a): 2674-2680 (in Chinese).

Relatively stable scaly protective layer forms in the combustion region surface, in addition, the total lost mass of SYNER

gistic Flame Composite is higher. With those variety of factors, the flame retardancy effect of the synergistic flame Composite is higher. The HM-Mg(OH)₂/PE flame retardant Composites pass the UL-94 Vb13 rating with LOI value of 28%, and the tensile strength reaches 8 MPa when mass ratio of HM to Mg(OH)₂ is 1:2 with 60 wt% loading.

Keywords: hydromagnesite; Mg(OH)₂; synergistic flame retardant; Composites; Cone calorimetric

Brucite (hydromagnesite, HM) is a magnesium mineral. The main ingredient of it is hydrated alkali magnesium carbonate. HM mineral plus work simple. In recent years the application of HM is increasing, mainly to apply domain for preparation of Magnesia, Basic Magnesium carbonate, etc., additionally report point to, HM has a wide application in the field of fire-retardant foreground^[1-3].

HM The fire-retardant mechanism of and Mg(OH)₂ similar^[4-5], HM the ability to release water and under thermal action CO₂, these decomposition release process can absorb a lot of heat, to reduce flame retardant polymers material surface flame temperature, Delaying its degradation or making it difficult to burn; same When the water vapor and CO₂ can override flames, Burn down area combustible gas and oxygen concentrations; also decompose remaining MgCO₃, Mg(OH)₂ and MgO etc can be on polymer surface to form a heat transfer barrier layer, block continuation of polymer matrix so-

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lution^[6-7]. But related research also indicates that, HM flame Retardant less efficient, and high proportion of HM bound to

cause polymer material the mechanical properties of the material drop significantly^[8-9].

HM fire Retardant as a flame retardant is relatively low, is large level is due to HM decomposition temperature is too low cause of, can take the Mg(OH)₂ vs HM Duplicate, use the HM-Mg(OH)₂ Composite blocking The Synergy in the decomposition of the fuel agent, get lower cost, performance is more OK HM-Mg(OH)₂ co-polyethylene (PE) Flame Retardant composite.

1. Experimental materials and methods

1.1 Raw Material

HM, size Dis Ten⁴m, Jiangsu Sibeli new material has Limited Company; polyethylene, (8) s, Lanzhou Petrochemical; Mg(OH)₂, granularity 5 to 15 μm, Shandong Dongying Ocean Chemical Co., Ltd..

1.2 hm-mg (OH)₂ Collaboration PE Preparation of flame retardant composites

will HM and Mg(OH)₂ follows the table 1 proportional to with, mix evenly in high speed mixer and sift, made HM-Mg(OH)₂ Composite flame retardant.

Double screw extruder (haake poly lab OS, beauty Thermo Fisher Technology Co., Ltd.) Preparation of flame retardant quality fraction to 5 wt% and 10 wt% Fire-retardant for PE Composite, Extrusion temperature degrees 165~175°C, rotate Speed r/min. with Huck mini injection molding machine (haake mini jet, United States Thermo Fisher Technology public Division on 175C, 50 MPa injection molded into standard test under injection pressure spline.

tests and representations

thermogravimetric

Analysis (Thermal gravimetric analysis, TGA): take

approx 5~10 mg samples, with Netzsch TG209F1 Hot-weight Analyzer, with 10°C/min The speed of the is from room temperature Upto 1000°C, to test the thermal weightlessness of the sample in an air atmosphere behavior.

Limit Oxygen index: Follow the GB/t 2406.2-2009^[1]. Enter line, Using Oxygen Index Analyzer (HC-2 type, Nanjing Jiangning District, Instrument factory) test specimen limit Oxygen index.

Vertical Combustion: Follow the GB/t 2048-2008^[all], mining with vertical combustion tester (czf-3 type, Nanjing Jiangning District Analysis instrument factory) test specimen vertical combustion performance.

extrude Performance: Follow the GB/t 1040.1-2006^[1] on, using Universal Mechanics test machine (CMT5504 type, Think twice about Shenzhen Material Test Co., Ltd. test specimen tensile Properties.

Cone calorimeter: Reference ISO 5660^[1], sample size 50MMX50MMX3mm, Thermal radiation intensity is kW/m², using cone calorimeter (FTT, United Kingdom Tensilica (G)) test try-like burning behavior.

2. Results and discussions

2.1 HM-Mg(OH)₂ decomposition behavior of composite flame retardants

diagram 1 is HM, Mg(OH)₂ and HM-Mg(OH)₂ Complex Heat-heavy curve of flame retardant in air. from Diagram 1 (a) can see out, Two inorganic compounds have a significant weightlessness in the heating process, where Mg(OH)₂ in 305~421°C concentration weightlessness between: 4; and HM The thermal weightlessness of is mainly divided into three stages: in 191~352°C weightlessness 2%; in the 352~492°C weightlessness 33% in 492~C weightlessness 46%. when 8 (8) CHM weightlessness Total compared to Mg(OH)₂ High 8, Visible HM as fire retardant not only releases more flammability during combustion

diagram 1 Brucite (HM), Mg(OH)₂ (a) and brucite-Mg(OH)₂ Composite

Flame Retardant (b) Hot-weight curves for (warming rate 10°C/min, room temperature ~800°C, Air)

Fig. 1 Thermal Gravimetric analysis Curves of Hydromagnesite

(HM), Mg(OH)₂ (a) and NM-mg(OH)₂ synergistic flame

Retardant (b) (10°C/min, room temperature-800°C, Air)

gas to suppress the occurrence of combustion, and the temperature range of the effect is more wide. But HM start decomposition temperature low, 191~352°C interval. Structural water released within is easy to create as a polymer flame retardant. Chengki Body Foaming, but may increase polymer contact with air area, accelerating burn occurrence^[1], and HM in 352~492°C. The primary decomposition of the is that the decomposition release is higher than the HM, but divided by solution temperature comparison Mg(OH)₂ slightly higher, its flame retardant validity may be affected by to affect. To improve the fire-retardant effects of the HM, can be HM with Mg(OH)₂ duplicate, To Adjust the composite flame retardant by mixing proportions decomposition features, play a synergistic effect.

from Diagram 1 (b) to see, decomposition behavior of complex flame retardants combined with HM and Mg(OH)₂. Decomposition characteristics of two components, Subdo not 190~310°C, 310~420°C, 420~460°C, 460~530°C and 570~660°C appears 5a different interpretation put stage, where 310~420°C and 420~460°C at the should HM and Mg(OH)₂ Primary decomposition of, Two decomposition peaks to each other. The coincide to form Shuangfeng. will HM vs Mg(OH)₂ forte as flame retardant Agent, to reduce the Mg(OH)₂ blocking caused by mass decomposition in cryogenic zones flame Retardant effect lower, also extend flame retardant in 300~450°C time for the continuous release of the fuel-free body in the scope, in When a polymer burns, take more heat., Postpone burning development.

2.2 hm-mg (OH)₂ Collaboration PE decomposition of flame retardant composites behavior

Diagram 2 is HM-Mg(OH)₂ Collaboration PE Flame Retardant composite HM, MH, HM1MH1 and PE in an atmosphere of Ten°C/min rises from room temperature to 800°C. Hot-weight curves for can look at goto, Mg(OH)₂ Flame Retardant PE. The decomposition of composites is divided into two phase, First in 3h°C in composite when Mg(OH)₂ start decompose to release water vapor and 403°C peak near, this decomposition The procedure can suppress the composite when it is lit PE Burn Burn effect. with Mg(OH)₂ flame-retardant PE Composites Mg(OH)₂ explode near complete, Composite's PE start accelerated decomposition and combustion, total decomposition speed slightly lower quickly, on 442°C peak near. Mg(OH)₂ flame retardant PE complex composite material decomposition process Mg(OH)₂ flame-retardant PE Composite material material decomposition start decomposition temperature lower, Only 191~352°C. To lose the quality 9%, This decomposition process is in the suppression matrix. The effect of material combustion is limited, actually composite material Weightlessness in this phase is higher than in composites HM theory weightlessness 792%^[7], may be due to HM decomposition causes composite table surface foaming, Increasing and constantly updating PE Contact Air interface promotes PE decomposition. on 385~425°C scope, HM blocking burn composites HM start decomposition, and on the decomposition level End of paragraph, composite decomposition release rate compared to this phase peak

400 temperature/°C diagram 2 Brucite-mg (OH)₂ synergistic polyethylene flame retardant composites

Thermal weightlessness curve (warming rate 10°C/min, room temperature ~800°C, Air)

Fig. 2 Thermal Gravimetric analysis Curves of hydromagnesite-

Mg(OH)₂ Synergistic Flame Retardant polyethylene composites

(10°C/min, room temperature-800°C, Air)

value dropped significantly, in 425°C decreases the thermal weightlessness rate of composite to %/min³, and then goto the PE break-main decomposition speed up phase, and Composite in PE explode peak value temperature comparison Mg(OH)₂ flame retardant composite improved 10°C, visible, HM In addition to being able to produce difficult gas body blocking combustion occurs outside, its decomposition phased product to PE. The decomposition of can also take the inhibition^[1]. compared to HM Fire-retardant PE composite, HM1MH1 Co-PE flame-retardant Composites in 191~352°C Zero weight loss between only 6.4%, also divided by after the flame retardant has been decomposed interpretation drop rate significantly decrease, PE Peak decomposition temperature of in Step increase reach 462°C. visible HM vs Mg(OH)₂ with good synergistic flame Retardant, to reduce composite at low temperature area Invalid decomposition, can also be retained HM decomposition products to PE decompose inhibition.

2.3 HM-Mg(OH)₂ Collaboration PE Flame Retardant composite heat release rate

Diagram 3 is HM-Mg(OH)₂ Collaboration PE Flame Retardant composite HM, MH, HM1MH1 and PE hot-release in cone calorimetry drop rate (Heat release rate, HRR) and Total heat release (total heat release, THR) over time curve, Table 2 is the corresponding data for the cone thermal curve. Combined with a chart to see out, add flame retardant composites compared to pure PE up to 548.3 kW/m². The peak heat release rate is significantly lower for where, HM flame-retardant PE composites with Mg(OH)₂ flame retardant PE compound Material A. Maximum hot release rate pkhrr1 (Peak Heat release rate 1) are all less than 5 kW/m². Around, but HM Fire-retardant PE Peak heat release of composite material appears earlier, its lighting time (time to ignition, TTI) only 3s, compared to pure PE 5s more advanced. This may be due to a cone calorimeter test with a in HM start decomposition at lower temperature, Explode release gas causes PE Matrix Foaming Volume expansion, Expansive materials The surface is exposed earlier. The spark ignition device of the cone calorimeter from this lit. [1]. Pure PE due to low temperature decomposition gas less, anti- and TTI longer. Mg(OH)₂ flame retardant composites TTI long up to 5s, This may be the same as Mg(OH)₂. The low temperature stability of has closed. HM1MH1 Composite Fire-retardant PE Composite due to HM contains less, burn time compared to HM flame retardant composites extended to 10s, and its pkhrr1 is only 5.5 kW/m², for several duplicate material lowest. Mg(OH)₂ flame retardant PE Thermal release of composites The curve is more like a top-leaning trapezoid, Its second largest hot release rate peak pkhrr2 (Peak Heat release rate 2) not obvious, HM flame retardant composites and HM1MH1 Fire-retardant PE Composite HRR The curve is similar to M Shape, reference The in the hot-weight test

A reduction in the rate of weight loss of composite materials after the decomposition of the flame retardants, M The heat release peaks may be generated by HM The decomposition product suppresses the PE The results of matrix decomposition. Both pkhrr2 are lower than their pkhrr1, HM1MH1 Fire-retardant PE Composite pkhrr2 more low, is only 113.5 kW/m². Compare The total amount of heat released by the to see, The addition of a flame retardant significantly reduces the Total amount of heat released by the pre-3(8) seconds material, where HM1MH1 Fire-retardant PE Composite Minimum, is only 1 MJ/m², compared to pure PE 6 MJ/m² drastically reduces 1%. When irradiation, to reach 600s, flame retardant composites with pure PE the THR Gap between is narrowing, This is mainly due to the flame retardant of inorganic flame retardant mechanism decision of, inorganic flame retardants are mainly produced by decomposition of non-flammable gas suppression initial burn occurrence, But when inorganic decomposition complete after "", "" inorganic oxides residual organic oxide high thermal conductivity, very, hard to form a good insulating layer [a], Therefore in the cone-heat continuous High radiation intensity, The combustible components in the final composite are decomposed burndown.

Diagram 4 is three HM-Mg(OH)₂ Collaboration PE Flame Retardant composite material cone weight thermal test sample photo. Visible, Test End After most samples are white, almost no carbide generation, need Note, Mg(OH)₂ flame Retardant composite cone calorimeter test the sample after forms a seemingly complete compact surface, but like Product Center has a huge collapse, Description of the production of dense surface no block surface lower PE continued decomposition of the matrix combustion [7]. With HM fire-Retardant PE Composite after test render loosely crushed table Face status, corresponds to the worst fire-retardant effect of the three., but broken The appearance of the surface may also indicate that HM decomposition products and PE Matrix and the the decomposition products form some kind of composite structure, This structure as a The whole was destroyed by intense irradiation at the end of the cone heat test. a. HM1MH1 Fire-retardant PE Composite presented after test Scale-like surface structure with cracks, This structure is both in the To degree To maintain shape integrity, simultaneous sample deep decomposition production the Raw gas does not gather in the center., Causes a large surface of the protection layer product break, This could be HM1MH1 flame retardant PE composites for better performance in cone calorimeter test [20], also explains HM and Mg(OH)₂ has good synergy in the flame retardant process Action.

2.4 HM-Mg(OH)₂ Co) PE mechanics of flame-retardant composites performance and flame

retardant performance

Table 3 is HM-Mg(OH)₂ Collaboration PE Flame Retardant composite

HM, MH, HM1MH1 and PE Limit Oxygen index for, Vertical burn performance and tensile strength data can see, add 50wt% and 60WT% flame retardant composites all have better fire-retardant performance of, its vertical combustion performance is up to UL-94V-0 level, Mg(OH)₂ and HM-Mg(OH)₂ Collaboration PE flame retardant complex. The Limit Oxygen Index of the material in the flame retardant content is 50, doesn't [%] * [%] reached 25%, compare to content HM fire-retardant PE composite High 2, compared to pure PE increased 8%. Mg(OH)₂ and HM-Mg(OH)₂ Collaboration PE The limit Oxygen Index of flame-retardant composites in flame retardant content? wt% is further enhanced to 28%, Phase Compare same content HM Fire Retardant PE Composite High 2, Compared to pure PE increased 11%.

tensile strength display, Add HM fire-retardant for PE composite tensile strength compared to pure PE 3MPa big drop, and Mg(OH)₂ fire-retardant PE composite tensile strength compared to pure PE increases, to add the same amount of, HM1MH2 fire-retardant PE composite with Mg(OH)₂ Flame Retardant PE Pull for composites Extended strength is basically the same, and the tensile strength of the composite fire retardants HM decrease gradually as the content increases. overall considering Mineral Source HM compared to Mg(OH)₂ cost Lower, one equal limit oxygen index and close tensile strength, with HM vs Mg(OH)₂ flame retardant for reducing the cost of flame-retardant materials Good effect.

Table 3 Brucite-mg (OH)₂ mechanical properties and limit oxygen index of polyethylene flame retardant composites
Table 3 mechanical properties and Oxygen index of HYDROMAGNESITE-MG (OH)₂ synergistic flame retardant Polyethylene composites

3. Conclusion

(1) Brucite (HM) as a flame retardant although more flammable gases can be released to suppress burning of the fire in a burn through, but due to low initial decomposition temperature, on composite burn the initial reaction will be counterproductive. will HM vs Mg (OH)₂ reuse uses to decompose within a wider combustion temperature range to better flame retardant, is more than HM use flame retardant alone greatly increased, and in the Limit Oxygen index and tensile strength unchanged on premise, flame-retardant polyethylene (PE) composite cost significant down.

(2) when HM and Mg (OH)₂ with a quality ratio of 1:2 Collaboration and the total quality of the composite is reached? wt% when, HM-Mg (OH)₂ Collaboration PE the limit Oxygen index of flame retardant composites is 28%, vertical combustion level reaches UL-94V-0 level, tensile strength reach 8MPa.

(3) Although HM-Mg (OH)₂ heat loss for composite flame retardants heavy behavior Performance HM and Mg (OH)₂ individually decomposed plus and, but on HM-Mg(OH)₂ co-fire-retardant PE composite, Two kinds of flame retardants show good synergy. HM and Mg (OH)₂ synergistic Fire-retardant mechanism: The composite flame retardant is low HM The content causes the composite to ignite the initial invalid or even negative face decomposition reduction, But composite flame retardants can keep HM decomposition Products against PE inhibition of matrix high temperature decomposition, can also burn burn area surface to form more stable and less damaging scale like protection Layer, plus composite flame retardant overall higher total decomposition release rate, more factors work together, Improve the flame-retardant effect of composites.

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