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Magnesium Hydroxide and Magnesium Oxide in Oxidation and Burning of Polypropylene

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Authors' contributions

This work was carried out in collaboration between all authors. Author JR designed the study, performed the analysis and wrote the first draft of the manuscript. Authors MH, LR, IJ, KC and IC managed the analyses of the study. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

Magnesium hydroxide eliminates DSC exotherm of polypropylene oxidation and thus the peroxidation process. At the same time, non-isothermal thermogravimetry experiments show that the temperature of the maximum rate of volatiles released due to polypropylene decomposition is significantly higher than that from original polypropylene. It appears that in the presence of magnesium hydroxide, the degradation products are not formed predominantly from decomposition of peroxides but from direct scissions of polypropylene chains. Chemiluminescence experiments confirmed that magnesium ions in alkaline conditions have the activating effect on oxygen from surroundings contributing thus to the more pronounced oxidation of soot and to the decrease of the smoke released during polypropylene burning. The links with the burning of the polypropylene with alkaline magnesium compounds were searched.

Keywords: Magnesium hydroxide; magnesium oxide; differential scanning calorimetry; thermogravimetry; chemiluminescence; heat release rate; cone calorimeter.

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1. INTRODUCTION

Magnesium hydroxide belongs to inorganic filler imparting to polymers flame retardant properties. To achieve a satisfactory flame retardant effect, relatively high filling amount of magnesium hydroxide has to be used that may have the negative impact on the resulting material properties. The effect of magnesium hydroxide on the flammability pattern of polypropylene is predominantly of physical character including (a) endothermic decomposition of magnesium hydroxide providing water (b) diluting effect of an additive load on the amount of flammable material (c) diluting effect of water on the flammable volatiles and d) the effect of solid oxide on the heat transfer from the gaseous phase to the surface of burning polymer. However, direct interactions with the polymer and with other additives are also expected as fillers usually reduce the stability of the original polymers [1-4]. The flammability of the polypropylene mixtures with magnesium hydroxide has been studied using the cone calorimeter [5-12].

Regardless of the fact that the effect of magnesium hydroxide and magnesium oxide on various polymers was largely examined, the number of queries remains that are worth of further study. They concern particularly of the direct interaction of the filler with polymer when exposed to heat and of the comparison of the effect of magnesium hydroxide and magnesium oxide on polymers flammability. The search for the links between the smoke suppression during polymer burning and the effect of magnesium hydroxide and magnesium oxide on the polymer oxidisability are also worth of further study.

In this paper, the non-isothermal thermogravimetry (TG) and differential scanning calorimetry (DSC) experiments performed with milligram quantities of polypropylene loaded with magnesium hydroxide have been attempted in order to search the relations with cone calorimetry measurements. The characterization of the polypropylene blends from the viewpoint of their oxidisability has been assessed by the non-isothermal chemiluminescence. The flammability of the mixtures of polypropylene with magnesium hydroxide and magnesium oxide was characterised by cone calorimetry on thermally thin samples of non-standard sizes.

2. MATERIALS AND METHODS

2.1 Chemicals

The samples were characterised as follows:

Mg(OH)₂, Magnifin H10, high purity grade for applications in flame retardancy, specific gravity 2.35 g/cm³ was purchased from Albermarle/Martinswerk.

Platelets of a thickness 2 mm were prepared by compression molding at 230°C from mechanically mixed powders of magnesium hydroxide with polypropylene Tatren HF322 (specific gravity 0.91 g/cm³, the melt flow index 2.16 g/10 min., free of calcium stearate). The polymer contained small amount (0.1% w.) of the processing stabilizer (ionol) that could not affect the flammability performance of the polymer.

MgO, light, air and moisture sensitive was purchased from Aldrich Chemical Co. Inc.

Powdered mixtures of MgO with polypropylene (Slovnaft Bratislava, polypropylene was free of stabilizers, the melt flow index was 22.4-29.6); the corresponding loads were prepared by mechanical mixing.

2.2 Instruments

DSC measurements were performed using a Mettler Toledo DSC 821^e apparatus. Indium was used for calibration of temperature and heat of fusion. Thermooxidative decomposition was investigated in a temperature range from room temperature up to 500°C (5°C/min) in air flow (50 ml/min). The amount of samples was around 3 mg.

TG measurements were performed using a Mettler Toledo TGA/SDTA 851^e instrument in a air flow (30 ml/min) using a heating rate of 5°C/min in a temperature range from room temperature up to 550°C. Indium and aluminium were used for temperature calibration. The amount of samples used was around 3 mg.

Chemiluminescence (CL) measurements were performed with a photon-counting instrument Lumipol 3 manufactured at the Polymer Institute of the Slovak Academy of Sciences. The sample was placed on an aluminium pan in the sample compartment. The oxygen flow through the sample cell was 3.0 l/h. The temperature in the sample compartment of the apparatus was raised from 40 up to 250°C, with a linear gradient of 5°C/min. The signal from the photocathode was recorded after each 10s of data collection as an average value of 10 readings. The amount of samples used for each measurement was in the range of 4.5-5 mg.

Dual cone calorimeter was the product of Fire testing technology, England. For thermally thin polymer powders with additives a special rectangular holder (83 cm^2) was manufactured from stainless steel 9.1x9.1x 0.3 cm. This holder was placed into the main holder supplied by cone calorimeter producer. The bottom of the holder was isolated from the main holder by 5 mm thick layer of kaowool. The centre of the samples was situated 6 cm from the lowest part of the cone heater.

One should note that the measurements of thermally thin (thickness<6 mm) and/or powdered samples do not follow ISO recommendations [9-11]. However, it has some advantages as it saves the time and material [13] and provides larger flexibility in sample preparations as e.g. various blends of polymers with fire retardants and other additives.

The heat release rate was calibrated by burning of methane.

The temperature of the cone which corresponds to a certain cone radiancy was set according to the calibration diagram determined by the use of radiometer for a distance of the sample from the cone edge 6 cm.

IKA calorimetric bomb C 200 has been used for determination of gross heats of combustion in oxygen, pressure of oxygen 30 bars.

Limiting oxygen index (LOI) was determined on standard equipment as the minimum concentration of oxygen in the mixture with nitrogen at which the flame still burns.

2.3 The Evaluation of Nonisothermal Thermogravimetry Runs

The formation of volatile degradation products as observed by non-isothermal thermogravimetry represents an integral process. The complex non-isothermal thermogravimetry curve that is apparently composed of several independent processes was described by the first-order scheme, i.e. $-\frac{dm}{dt} = km$. In a non-isothermal mode,

$$-\frac{dm}{mdT}\frac{dT}{dt} = A\exp\left(-\frac{E}{RT}\right),\tag{1}$$

where $\beta = \frac{dT}{dt}$ is a linear heating rate. After integration, we obtain

$$m = m_0 \exp\left[-\frac{A}{\beta} \int_{T_0}^T \exp(-\frac{E}{RT}) dT\right]$$
 and for the process composed of j temperature

dependent components - "waves", we have

$$m = m_0 \sum_{i=1}^{j} \alpha_i \exp\left[-\frac{A_i}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E_i}{RT}\right) dT\right].$$
(2)

Provided that mass changes are expressed as a percentage of the original mass, m_0 , triplet of parameters α_i, A_i, E_i may be found for polypropylene (i=1), inorganic additive (i=2) and the polymer residual mass (i=3) decomposition by a nonlinear regression analysis program. The program was applied to the experimental mass m vs. temperature T records, from the initial temperature T_0 (laboratory temperature) to a final temperature T (550°C) of the experiment.

3. RESULTS AND DISCUSSION

3.1 Non-isothermal Chemiluminescence, Thermogravimetry and DSC of Polypropylene with Magnesium Hydroxide

Comparing DSC record of pure polypropylene with that containing 30% of magnesium hydroxide we may see that almost no hydroperoxidation occurs in the polypropylene loaded with magnesium hydroxide. (Fig.1, lines 1 and 2). Due to magnesium hydroxide a typical DSC exotherm of oxidized polypropylene disappeared and was replaced by the sharp exotherm occurring at considerably higher temperatures (Fig.1, line 2). This exotherm coincides with the ignition of the sample.

At the same time, the non-isothermal thermogravimetry patterns in air for samples of polypropylene containing $Mg(OH)_2$ are also typical with the shift of the temperature of the maximum release of volatiles to higher values (Fig.1, line 2a) confirming that hydroperoxides

are not the main source of volatiles during degradation of polypropylene in the presence of $Mg(OH)_2$.



Fig. 1. Comparison of nonisothermal DSC (1, 2) and differential thermogravimetry (1a, 2a) records of polypropylene (1,1a) and polypropylene with 30 wt. % of magnesium hydroxide (2,2a) in air. The rate of heating 5°C/min

While for polypropylene this temperature is 291°C, for polypropylene with 10% of Mg(OH)₂ it is already 379°C for 30% of Mg(OH)₂ 385°C and for 40% of Mg(OH)₂ 389°C. At these loads the release of flammable degradation products from polypropylene that precedes that of water from Mg(OH)₂ becomes kinetically not well distinguished and both processes mutually coincide. Very sharp slope on the TG record for loads 40 and 50% of the weight corresponding almost to 90°C (Fig.2, arrow A) indicates that the contribution of the heat from the ignited sample should be involved. Due to this heat the TG system temporarily gets out of the temperature control. At the concentration of Mg(OH)₂ both processes (i.e. release of lower value (376°C) while for higher contents of Mg(OH)₂ both processes (i.e. release of water and polypropylene degradation products) are visually well separable with the temperatures of the maximum rate of products release 320 vs. 348°C and 253 vs. 355°C for 60 and 70% of Mg(OH)₂, respectively (Fig. 2). This is also an evidence that at this high loads there occurs the reverse phase separation of polypropylene from Mg(OH)₂. The DSC and DTG records quite well agree as it concerns of the corresponding extreme values (Fig.1).

The records of the mass loss from the Fig. 2 were analyzed using the equation 2 enabling to separate the decomposition of respective components of the blend (Table 1). It may be seen that while pure polypropylene looses its degradation products in a process having the activation energy around 180 kJ/mol, polypropylene with magnesium hydroxide gives the activation energy considerably lower - 50kJ/mol. At the highest loads of $Mg(OH)_2$ the value of activation energy increases again as separation of hydroxide from polypropylene occurs and some part of polypropylene decomposes without direct interaction with magnesium hydroxide. The value in the brackets in Table 1 denotes the portion of the decomposition of

respective component in % as determined by the calculation. It is worth of noting that decomposition of magnesium hydroxide into water and MgO having activation energy around 260 kJ/mol coincides with the third process and is superposed with the degradation of soot potentially formed in polypropylene decomposition.



Fig. 2. The nonisothermal thermogravimetry runs in air for polypropylene with Mg(OH)₂, the rate of heating 5°C/min. The numbers denote the initial concentration of Mg(OH)₂ in wt.%. Points represent the examples of the fit of the non-isothermal thermogravimetry course by the eq. 2 for the sum of the three first order decomposition processes (j=3). Arrows A point to the steep slope of the experimental run.

When examining the non-isothermal chemiluminescence runs for polypropylene with alkaline magnesium compounds we obtain surprisingly much more intense chemiluminescence intensities when compared to pure polypropylene. The experimental lines have a typical maximum that is situated at 217°C for lower loads of magnesium hydroxide and goes to the temperature around 197°C at loads 50 and 60%. A small increase to 201°C was found for samples with 70 wt. % of the filler (Fig. 3). The significantly more pronounced light emission from polypropylene containing magnesium compounds when compared with pure polymer was not reported until now. It may have its origin in alkaline character of additive and in interplay of reactions of hydroxyl ions, hydroxyl and hydroperoxyl radicals finally leading to superoxo anionradicals attached to the surface of the magnesium oxide according to the Scheme 1. The similar observation was done with non-stabilised polypropylene powder and MgO addition. Graph A of the Fig. 4 shows that magnesium compounds promote the faster occurrence and more intense light emission. The similar increase of the light emission was also observed in oxidation of cellulose in the presence of alkaline magnesium compounds [14].

% wt. of	Triplet of parameters for polypropylene			Triplet of parameters for Mg(OH)2			Triplet of parameters for residual mass		
Mg(OH) ₂	α ₁ , %	A₁, s⁻¹	E₁, kJ/mol	α2, %	A ₂ , s ⁻¹	E ₂ , kJ/mol	α3, %	A ₃ , s⁻¹	E ₃ , kJ/mol
0	88.7	8.8e14	184.3	-	-	-	-	-	-
10	57.1 (90)	4.2e3	73.6	34 (3.1)	9.2e18	261.6	10 (6.9)	8.5e3	115.1
20	39.1 (80)	9.1e1	54.8	45.6 (6.2)	1.1e19	261.4	16.2 (13.8)	7.3e3	115.8
30	17 (70)	5.5e1	51.6	60 (9.3)	4.3e18	260.6	22.8 (20.7)	3.8e3	115.9
40	13 (60)	5.2e1	51.9	57.7 (12.4)	3.0e18	260.0	30 (27.6)	2.7e3	115.9
50	14 (50)	3.1e1	50.1	50 (15.5)	6.8e18	260.6	37 (34.5)	2.4e3	115.7
60	32 (40)	5.7e8	123.8	22.6 (18.6)	7.0e10	161.2	45.5 (41.4)	6.2e-4	20.9
70	21 (30)	1.4e9	121.3	26.1 (21.7)	2.4e17	237.9	50 (48.3)	2.1e-4	26.9

Table 1. The deconvolution of nonisothermal thermogravimetry curves of polypropylene in air with Mg(OH)₂ into the sum of 3 first order reactions (equation 2). In brackets, there are portions of corresponding component as they follow from calculation



Fig. 3. The chemiluminescence (CL) intensity - temperature runs for different loads of magnesium hydroxide in polypropylene. The numbers denote the initial amount of Mg(OH)₂ in wt. %, the rate of heating was 5°C/min, oxygen. Polypropylene was stabilized with 0.1 % of the processing stabilizer.



Fig. 4. The intensity of chemiluminescence (CL) runs with temperature; comparison of stabilized and nonstabilised polypropylene and of the effects of MgO and Mg(OH)₂, oxygen. The rate of heating was 5°C/min. The graph A is the section for intensities of the light emission to 10,000 counts/s/1 mg

$$Mg^{2+} \xrightarrow{O-O'} HQ^{2+} \xrightarrow{O'} Q^{2+} \xrightarrow{O'} Q^{$$

Scheme 1. The proposal of the activating effect of magnesium compounds on the light emitted from oxidation of polypropylene

The chemiluminescence pattern from the above systems will be composed with the chemiluminescence from polypropylene itself (Scheme 2) that is one of the most studied polymers for easy examination of oxidation and related chemiluminescence [15-19].

The heat gain higher than 400 kJ/mol in an elementary reaction of radicals recombination was reported as the necessary pre-requisite of the light emission appearance if the light emission comes from excited triplet carbonyl groups.



Scheme 2. Chemiluminescence from the disproportionation of peroxyl radicals (Asterix denote the corresponding excited states)

In the above reaction, the excited triplet ketones and singlet oxygen may be formed due to synchronously released heat (450 kJ/mol).

3.2 Ignition and Burning of Polypropylene with Magnesium Hydroxide and Magnesium Oxide in Cone Calorimeter

Apparently there is no direct link between the results of thermooxidation experiments and ignition and burning of polypropylene containing magnesium compounds. Especially in the case of burning when the process of degradation of polypropylene melt is assumed to occur under anaerobic conditions. It appears, however, that both sets of data may be linked particularly via the mechanism of smoke suppression. As it was reported by Hornsby [20] the

oxides produced by decomposition of magnesium hydroxide at higher temperatures are very active materials having the high surface area that may readily absorb species, as e.g. carbon rich compounds which form the nucleation sites of the formation of soot and smoke during the burning process. The formation of the carbon rich particles C (Scheme 3) starts with the switch between the reaction of addition of alkyl radicals to oxygen with formation of alkyl peroxyl radicals and the reaction of disproportionation leading to hydrogen peroxyl radicals and unsaturated structures on the polymer chain. This is usually observed at temperatures above 300°C. The representatives of such carbon rich particles C are acetylene and benzene in gaseous phase and carbon residue in the condensed phase.

$$\begin{array}{ccc} -CH_2-CH_2^{\cdot} + O_2 \longrightarrow -CH_2-CH_2 + HO_2^{\cdot} \\ & & \downarrow \\ & & \downarrow \\ C \\ HO_2^{\cdot} \longrightarrow HO^{\cdot} + O \\ C + OH \longrightarrow CO + H^{\cdot} \end{array}$$

Scheme 3. The initial steps in the formation of carbon rich molecules in burning of polymer

The total smoke released during burning of polypropylene decays when increasing the content of magnesium hydroxide in polypropylene to 40% of the weight with a certain slope (Fig. 5). Above this load, however, the total smoke released has a higher slope finally achieving the value around 5 m²m⁻²g⁻¹ for the sample having 70 wt. % of Mg(OH)₂. It appears that till 40% of the load diluting effect of additive reducing the smoke predominates while at higher loads the supporting mechanism of the carbon oxidation from the active magnesium oxide surface comes into a play as well.



Fig. 5. The smoke release (SR) and total smoke released (TSR) during burning of polypropylene with Mg(OH)₂, the cone radiancy 35 kW/m². Numbers denote wt. % of Mg(OH)₂.

The effect of the initial weight of polypropylene on time of ignition deserves some comment. Up to the initial mass 15 g we may observe the significant discrepancies between time to ignition of polypropylene powder and polypropylene platelets. Polypropylene platelets gave considerably larger time to ignition when compared with powder (62 s vs. 37 s, Table 2), which is due to the fact that the mass of the polypropylene in platelet is more than two times lower than that in powdered systems. The dependence of time to ignition on lower initial mass of polypropylene may be explained by the necessity of accumulation of the critical concentration of flammable products above the surface of a polymer. For lower initial weight this time is apparently longer because of weaker stream of volatiles from the polymer melt into the gaseous phase.

It may be also seen that for the initial polypropylene weight above 15 g the time to ignition remains constant and is a good representative of the behavior of the thicker samples. Table 2 demonstrates it on the initial mass of polypropylene powder 23 g.

Comparing the heat release rate (HRR) for different initial weight of the PP powder we may see that for samples of lower initial mass (below 15 g) the peak of the heat release rate was lower too.

Both admixtures, i.e. magnesium hydroxide and magnesium oxide have significant reducing effect on the heat release rate from polypropylene burning (Fig. 6, Table 2) which becomes very pronounced at a relatively high loading of respective admixtures. When compared with $Mg(OH)_2$ where endothermic effect due to the release of water plays an important role, MgO reduces HRR as well. It is however, surprising that the reduction of HRR is even more distinct than that for magnesium hydroxide. This is again the indication of the important role of the effect of magnesium oxide on the melt reactions during polypropylene burning.



Fig. 6. The heat release rate runs for burning of polypropylene with Mg(OH)₂ (graph A) and MgO (graph B) in a cone calorimeter. The initial concentration of Mg(OH)₂ and MgO in polypropylene is in wt.% (numbers at a respective line), the initial mass of the sample is in the Table 2. Cone radiancy 35 kW/m².

From the LOI rating in the Table 2 we see that a significant increase to 33% can be obtained at such high loading of $Mg(OH)_2$ as 70% when the material is extremely brittle and also other mechanical properties are lost. The burning of polypropylene containing magnesium oxide and hydroxide is however, considerably more quiet when compared with pure polymer even

at as low loads of magnesium compound as 20%. This may be also due to the much better reflecting effect of MgO on the emissive heat from the flame than that from the metallic holder bottom. MgO remains on the bottom of the holder and the layer of the burning material is formed above.

Provided that we mix MgO with polypropylene powder to the total weight 15 g, the time to ignition is first reduced and starts to increase slightly at higher MgO loadings (Table 2). When working with PP platelets containing Mg(OH)₂, the initial mass of which is lower than that of the mixtures of MgO with PP powder, we observe the initial increase of time to ignition, however between 40 and 50 wt. % of Mg(OH)₂ a strong decrease was observed (Table 2). It seems therefore, that above 40% of Mg(OH)₂ there should predominate the catalytic effect of magnesium compound above the effect of water release.

The graphs comparing the mass loss from samples of polypropylene and magnesium hydroxide during burning and during the programmed increase of temperature by the rate 5°C/min may be seen in Fig. 7 A and B. The cone radiancy 35 kW/m² corresponds to the temperature in the centre of the cone 760°C. At the more developed process of burning the mass loss is slowed down due to the presence of Mg(OH)₂ similarly as the temperature of the maximum rate of the mass loss in TG is shifted to the higher values. The gross combustion heats as determined from calorimetric bomb decrease proportionally to the content of polypropylene in its blend with Mg(OH)₂ (Table 2).



Fig. 7. Comparison of the mass loss during burning (A) in a cone calorimeter (35 kW/m²) and non-isothermal thermogravimetry runs (B, 5°C/min) of polypropylene containing Mg(OH)₂, air. Numbers denote wt. % of Mg(OH)₂.

Sample	Initial weight in a cone Calorimeter experiment, g	Gross combustion heat from calorimetric bomb, J/g	LOI, %	t _{ign} , s	HRR peak, kW/m²
Polypropylene	6.5	48270	17.5	62	954
HF322, platelet	6.1			61	971
Polypropylene, powder	15			37	1070
Polypropylene, powder	23			36	1022
Polypropylene +10% Mg(OH) ₂	7.4	43343	17.7	71	849
Polypropylene powder +	15			22	409
16.6 % MgO				25	386
Polypropylene + 20% Mg(OH) ₂	7.6	38694	18.9	79	695
Polypropylene + 30% Mg(OH) ₂	8.1	34289	20.1	80	544
Polypropylene powder +	15			16	245.4
33.3 % MgO				17	271.3
Polypropylene + 40% Mg(OH) ₂	8.8	29187	21.1	78	417
Polypropylene + 50% Mg(OH) ₂	9.6	24250	22.4	43	353
Polypropylene powder +	15			15	176
50 % MgO				15	161
Polypropylene + 60% Mg(OH) ₂	10.9	19785	22.6	41	215.3
Polypropylene powder +66.6 %	15			16	127
MgO					
Polypropylene + 70% Mg(OH) ₂	11.1	15237	33.2	45	157.5
Polypropylene powder +	15			19	82.3
83.3 % MgO				23	75.6

Table 2. The main characteristics obtained from burning of polypropylene with additives (Mg(OH)₂ and MgO).. HRR is the heat release rate, LOI is the limiting oxygen index, the cone radiancy 35 kW/m²

4. CONCLUSIONS

- 1. Alkaline magnesium compounds (hydroxide and oxide) have strongly promoting effect on the light emission from polypropylene during its oxidation. The activation function of magnesium hydroxide or oxide on air oxygen was presumed having the link with the reduction of the smoke released.
- In the presence of magnesium hydroxide DSC exotherm brought about by hydroperoxidation of oxidised polypropylene disappears and formation of volatile decomposition products is shifted to higher temperatures. The reverse separation of Mg(OH)₂ from polypropylene may be observed for high loads of an additive.
- 3. Both magnesium hydroxide and magnesium oxide reduce the maximum heat release rate from burning of polypropylene. The effect of the MgO is even more significant than of Mg(OH)₂.

CONSENT

All authors declare that the consent was obtained from the respective approved parties such as the Institutions of the authors for publication of manuscript.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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