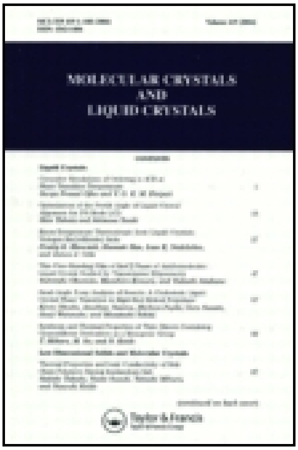

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The Flame Retardant for Polypropylene using Magnesium Hydroxide with Intumescent Components

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In this work we present results of our study on flammability of polypropylene samples containing various fire retardants. Moreover, the influence of the flame retardants added to PP on the structure of polypropylene matrix was investigated.

The effect of magnesium hydroxide on thermal properties of isotactic polypropylene was measured on a cone calorimeter. The measurements were performed in air at heat flux of $50 kW/m^2$.

Melamine polyphosphate, when added to MagShield-PP system, shows the highest fire-retarding effect compared to other intumescent compounds studied, such as pentaerythritol, urea polyphosphate and zinc borate. The weakest effect was recorded for zinc borate-containing composite.

Results of the structural study allow to conclude that fire retardants based on magnesium compounds in practice do not change the crystalline structure of isotactic polypropylene.

The intumescent fire retardants act as nucleants of hexagonal form of isotactic polypropylene.

Keywords: fire retardant; polypropylene; magnesium hydroxide; intumescent components; cone calorimeter

INTRODUCTION

Polypropylene (PP) is one of the oldest thermoplastic materials and one of the most important bulk plastics. A drawback of PP is, however, its flammability and smoke emission during its thermal decomposition. This fact makes a serious problem for further development of the production of the above plastic and its use for the manufacture of a large variety of commercial products.

The application of PP to building and textile industries results in an increased fire hazard, hence the growing importance of using fire retardants.

Three main of fire retardants are used for the reduction of polypropylene flammability:

- halogenated compounds (halogen-containing fire retardants),
- halogen-free compounds,
- intumescent systems.

Halogen-containing fire retardants are organo halides, chosen in such a way that their decomposition temperature is close to decomposition temperature of given plastic materials. Halogen (most frequently chloride or bromide), when present in the gas phase, reduces the concentration of high-energy free radicals, the formation of which is associated with the combustion process. By the elimination of free radicals, the intensity of combustion and the quantity of heat transferred to the plastic are decreased and this fact results in slowing down or complete suppression of the combustion of the plastic[1]. Halogen-containing fire retardant decomposes first which results in the evolution of bromine or chlorine. Then the liberated halogen reacts with combustion products this results in the formation of hydrogen halide. Bromine-containing fire retardants are usually more efficient than chlorine-containing ones because of a narrower temperature range needed for vaporisation which results in higher concentrations of fire retardant in the combustion zone. Compounds showing synergic effect, such as antimony oxides, lead to further increase in the fire-retarding efficiency of bromine and chlorine derivatives due to extension of the residence time of a halogen in the combustion zone [2] Unfortunately, polypropylene materials modified in such a way, during a fire evolve a lot of smoke as well as toxic and corrosive gas products which make fire-fighting more difficult. Hence a tendency is observed to abandon fire retardants and systems of this type.

Nowadays, more and more frequently halogen-free fire retardants are used for the reduction of polyolefin flammability. Hard-to-ignite polypropylene can be obtained by the introduction of a large quantity of mineral fillers (such as aluminium hydroxide, magnesium hydroxide and basic magnesium carbonate) which lose water during their thermal decomposition. The mechanism of fire-retarding action of these compounds consists mainly in condensed phase temperature reduction as a result of endothermic decomposition accompanied by the evolution of water which additionally dilutes polymer decomposition products. In order to increase the amount of fillers introduced to polyolefins, the fillers are frequently modified by the addition of polyfunctional silane monomers which improve the dispersion of a filler. Magnesium hydroxide is very efficient in limiting smoke emission from burning plastics, first of all due to the removal of heat from a plastic during its decomposition . Products of decomposition form a barrier around the plastic and bring about the formation of carbonaceous layer which retards the evolution of potentially combustible gases. Unfortunately, the large contribution (about 30%) of the fillers to the composition of modified plastic materials affect, as a rule, processing and physico-mechanical properties of the composite materials[5].

Very effective fire-retardants for thermoplastics appeared to be so-called intumescent systems which give them fireproofing properties by the formation of carbonaceous foam having a large volume and protecting underlying material from further action of flames [3]. The awareness of high hazard associated with the generation of large quantities of dense smoke and toxic or corrosive substances formed as a result of combustion (this hazard accompanies, as a rule, fire-retardant systems based on mixtures of halogenated compounds and metal oxides) has a stimulating effect on the studies of exploiting fire-retarding potential of intumescent systems added to polymers such as polyolefins[4]. However, the incorporation of an intumescent component into polymeric material is associated with several problems. First of all, the additives have to be thermally stable at polymer processing temperature and have to be compatible with polymer matrix in order to obtain good dispersion and low solubility in water to avoid hygroscopicity of polymeric material. The addition of intumescent substances to polypropylene brings about the formation of insulating foam during heating and this, in turn, retards the decomposition of plastic present under the foam layer as well as prevents from the evolution of toxic and combustible gases to a significant extent. Three components are necessary to achieve satisfactory action of intumescent systems:

- carbon-forming compound, e.g. polyhydric alcohol,
- esterification catalyst, e.g. ammonium polyphosphate,
- pore-forming agent, e.g. organonitrogen compound.

On other hand it is well-known that the addition of inorganic fillers like magnesium compounds to polypropylene can cause changes in the structure and properties of the composite resulted. Mechanical properties of the product depend on the adhesion energy between inorganic component and polymer matrix and on the structure of polypropylene matrix.

In this work we present results of our study on flammability of polypropylene samples containing various fire retardants. Moreover, the influence of the flame retardants added to PP on the structure of polypropylene matrix was investigated.

EXPERIMENTAL

The effect of magnesium hydroxide on thermal properties of isotactic polypropylene was measured on a cone calorimeter. The measurements were performed in air at heat flux of 50 kW/m^2.

The influence of different kinds and quantities of $Mg(OH)_2$ on fire properties of isotactic polypropylene-containing composites was studied using the systems as follows:

- polypropylene + magnesium hydroxide (20, 30, 35 and 40 wt % of MagShield S, MagShield M-SE, MagShield M-SA, MagShield M),

- polypropylene + 30 wt % of the following mixtures of MagShield with intumescent compounds:

  MagShield S (1 part by weight) - pentaerythritol (1 part by weight) - urea polyphosphate (3 parts by weight) [*sample IC1*]

  MagShield S (1 part by weight) - pentaerythritol (1 part by weight) - melamine polyphosphate (3 parts by weight) [*sample IC2*]

  MagShield S (2 parts by weight) - pentaerythritol (0.5 part by weight) - zinc borate (2 parts by weight) [*sample IC3*].

Methods of measurements

A. Efficiency of fire retardant action

Efficiency of fire retardant action of was studied by using a cone calorimeter. On the grounds of results of the measurements, the following fire properties of materials were determined by using computer-aided analysis:

◆ heat release rate	HRR	[kW/m^2]
◆ mass loss rate	MLR	[g/m^{2}s]
◆ total heat released	THR	[MJ/m^2]
◆ effective heat of combustion	HOC	[MJ/kg]
◆ time to sustained ignition	TTI	[s]

B. Structural analysis.

The structural investigation of prepared samples was carried out by means of a wide angle X-ray scattering (WAXS) method. CuK_{α} radiation (λ = 1,5418 Å) was used in the latter study. Superimposed multipeaks were resolved using the method proposed by Hindeleh and Johnson. upgraded and programmed by Rabiej. In this work experimental X-ray diffraction patterns are presented as upper curves and at the bottom of the figures separated lines of crystalline and amorphous phases are shown.

On the ground of separated diffraction lines the amount of β-form (k) in the samples of iPP was determined by using the Turner-Jones formula.

RESULTS AND DISCUSSION

Flame Retardancy

Polypropylene (PP) with the addition of MagShield magnesium hydroxide

It results from Figure 1, which shows heat release rate (HRR) for pure PP and MagShield containing PP samples, that the increase in Magshield magnesium hydroxide content, irrespective of the kind of $Mg(OH)_2$, leads to a strong reduction in HRR.

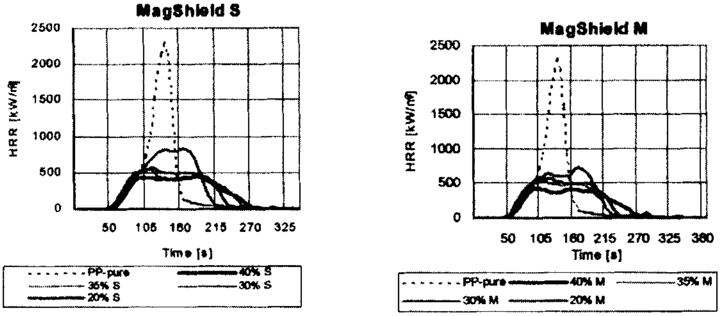


FIGURE 1. Heat release rate (HRR) recorded for pure PP and PP-MagShield composites

The peak of heat release rate (HRR_{max}) decreases from 2300 kW/m² for pure PP to about 450 kW/m² in the case of PP to which 40% of MagShield were added (Fig. 2).

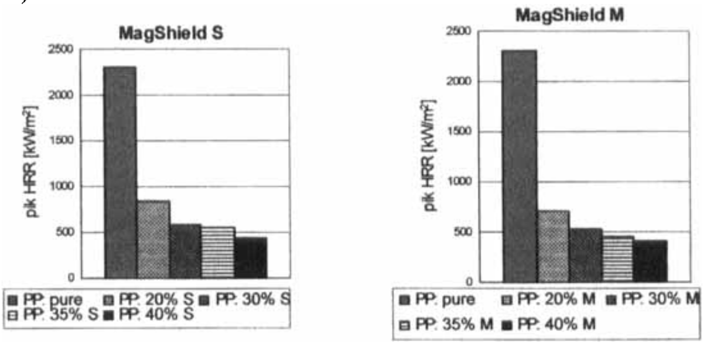


FIGURE 2. Peak heat release rate (HRRmax) for pure PP and PP-MagShield composites

The intensity of combustion of MagShield-protected samples is lower as shown by the shift in HRR curves towards longer time (Fig. 1). No significant differences are seen in the course of HRR curves recorded for samples with MagShield content ranging from 30 to 40%. The lowest $Mg(OH)_2$ content investigated (i.e. 20%) appeared to be efficient as well; HRR peak is present and no steady-state period is observed for heat release rate. Values of HRR_{av} calculated 180 seconds after the ignition of samples show the same tendency. The differences in HRR_{av} values (180 s) are small for samples containing 30 and more percent of MagShield compared to samples containing 20% of the above magnesium hydroxide (Fig. 3).

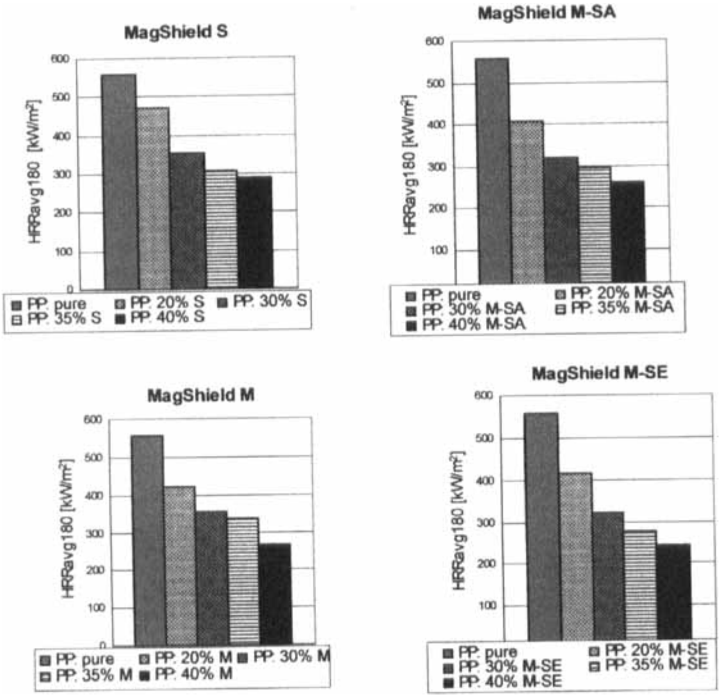


FIGURE 3. Average heat release rate measured 180 s after ignition (HRRav180) of pure PP

A comparison of mass loss rate (Fig. 4) with heat release rate (Fig. 1) shows that a rise in mass loss rate (MLR) is accompanied by an increase in heat release rate, but mass loss is observed earlier (10 s from the beginning of the measurement), whereas heat release was recorded only after the next 40 s. The difference can be caused by the fact that the loss of water and/or other volatile matter, which starts before the ignition of a sample, also contributes to MLR. The effect of MagShield on fire properties of the samples was also reflected in a decrease in total heat released (THR) and effective heat of combustion (HOC) and this effect became stronger with increasing amount of MagShield added to PP (Fig. 5).

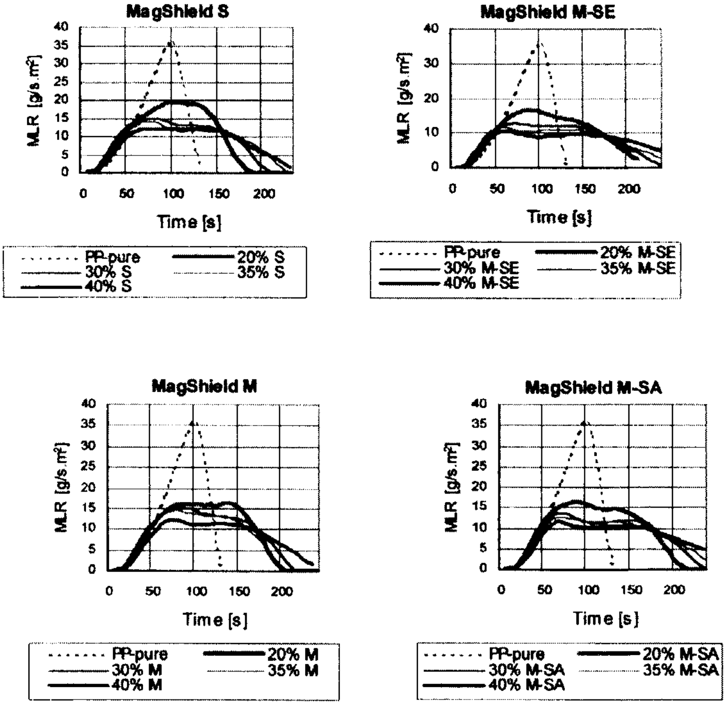


FIGURE 4. Mass loss rate (MLR) measured for pure PP and PP-MagShield composites

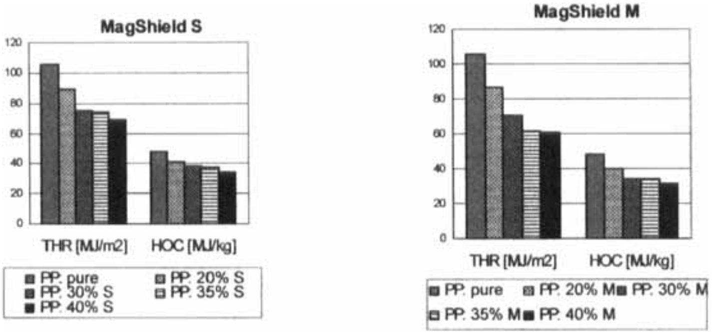


FIGURE 5. Total heat released (THR) and effective heat of combustion (HOC) recorded

Polypropylene with the addition of MagShield and compounds showing intumescent properties

The effect of different intumescence-causing compounds on the rate of heat release from MagShield-containing PP is presented in Figure 6. MagShield-zinc borate mixture is characterised by a strong increase in HRR and a clearly marked peak (HRR_{max}) is seen in the HRR curve. Moreover, the combustion time of zinc borate-containing PP is the shortest one measured during these experiments.

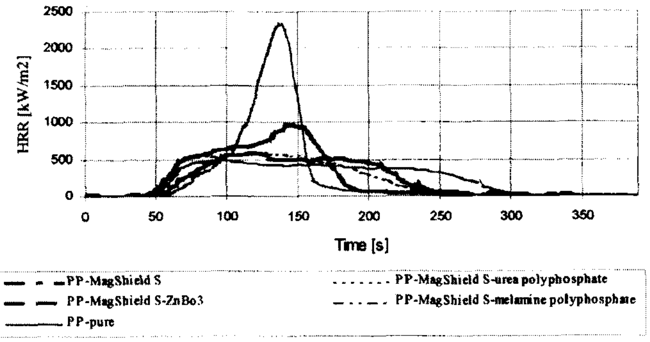


FIGURE 6. Heat release rate (HRR) recorded for pure PP and PP-MagShield-intumescent composites

A slight difference exists between HRR recorded for MagShield-PP composite and MagShield-urea polyphosphate-PP composite (Fig. 6). The most efficient compound from the point of view of reducing heat release rate appeared to be melamine polyphosphate. Heat release rate curves recorded for the system consisting of MagShield- melamine polyphosphate -PP are distinguished by the lowest HRR values and, after reaching HRR_{max}, heat is released with a constant rate for considerably longer time compared to other composites investigated. This points to a high fire-retarding effectiveness of the above system.

Wax Measurements

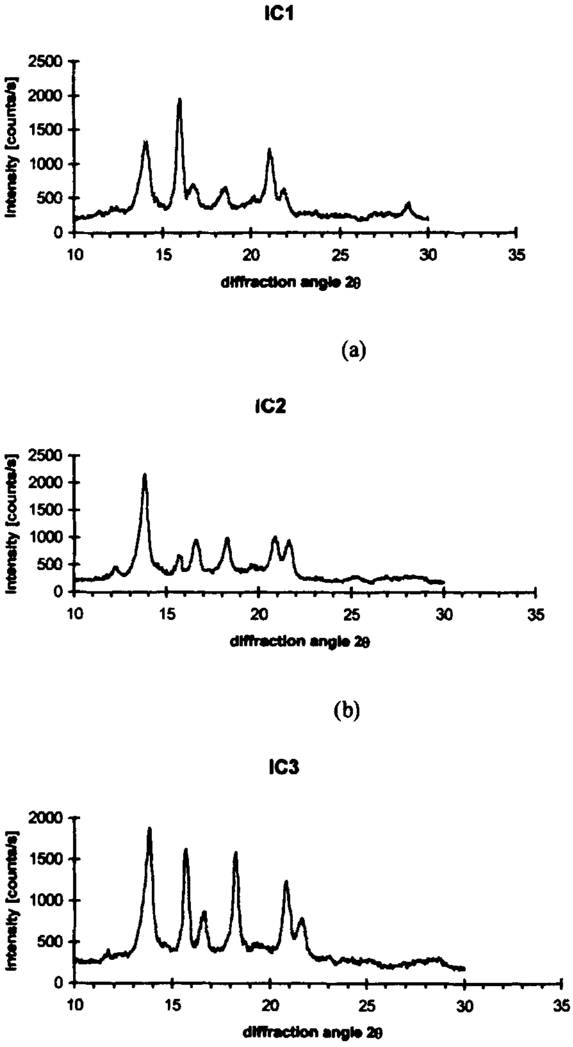
Two series of polypropylene samples containing 30% of fillers were analysed by X-ray diffraction method. The values of crystallinity degree (X_c) of isotactic polypropylene, determined on basis of separated diffraction lines, are listed in Table 1.

TABELE 1. Degree of crystallinity of retardant-containing isotactic polypropylene

Magnesium fire retardants	X_c [%]	Intumescent compounds (IC)	X_c[%]
iPP (pure)	62.7	-	-
iPP + MagShield S	59.1	iPP + IC1	58.4
iPP+ MagShield M	61.0	iPP + IC2	70.7
iPP + MagShield M-SE,	62.4	iPP + IC3	65.7
iPP + MagShield M-SA	66.4	-	-

The above data show that the addition of magnesium fire retardants changes the crystallinity degree of PP only by ±3% compared to pure iPP. However, in the case intumescent fire retardants (IC), the change in the degree of crystallinity is about 8 %.

Another interesting feature of intumescent compound-containing polypropylene samples was a change in the arrangement of iPP macromolecules. The addition of IC1 and IC3 resulted in the hexagonal form of iPP which was manifested by a significant diffraction peak at 16.12° of 2Θ (Figures 9 a-c).



(a)

(b)

(c)

FIGURE 9. X-ray diffraction patterns of PP-MagShield-intumescent compound systems
a/ IC1, b/ IC2, c/ IC3

CONCLUSIONS

1. MagShield has a beneficial effect on polypropylene combustion parameters. Its addition results in the decrease in heat release rate, mass loss rate, total heat of combustion and effective heat of combustion. The optimum amount of MagShield is about 30%.
2. Melamine polyphosphate, when added to MagShield-PP system, shows the highest fire-retarding effect compared to other intumescent compounds studied, such as pentaerythritol, urea polyphosphate and zinc borate. The weakest effect was recorded for zinc borate-containing composite.
3. Results of the structural study allow to conclude that fire retardants based on magnesium compounds in practice do not change the crystalline structure of isotactic polypropylene.
4. The intumescent fire retardants act as nucleants of hexagonal form of isotactic polypropylene.

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