COMBUSTION BEHAVIOUR OF PP-BASED COMPOSITES USED IN INDUSTRIAL PLASTICOLLAR®

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Abstract
The aim of this work was to improve the fire retardancy of the polypropylene-based composites used for production of plastic collars by Campia Imballaggi®. Therefore, the uses of phosphorous-containing flame retardant and magnesium hydroxide (MH) are discussed in terms of flammability behavior, thermal and mechanical properties. The flammability behavior of the PP-composites materials were investigated by means of techniques, such as Cone Calorimeter, Limiting Oxygen Index (LOI) and UL94 test.

1 Materials
Polymer matrices: polypropylene filled with 40% calcium carbonate (CCPP), and polypropylene filled with 40% talc (TPP) commercial grade material, supplied by Campia Imballaggi Company.
Flame retardant (FR): $Mg(OH)_2$ (Magnifin H5 GV - trademark) (MH) supplied by Albemarle Corporation, Exolit AP760 (Exolit) supplied by Clariant.

2 Samples preparation
Polymer matrices with flame retardant composites (Table 1) were prepared via direct melt compounding using a Leistritz ZSE 18 HP co-rotating twin screw extruder (L/D = 40). The operating temperature of the extruder was maintained at 225-220-217-215-210-210-210-205 ^{o}C from hopper to die, respectively. The screw speed was maintained at 150 rpm and the throughout was 3.5 kg/h. The molten material was quenched in water and then palletized.

Sample Code	CCPP wt.-%	TPP wt.-%	Exolit wt.-%	MH wt.-%
CCPP	100	-	-	-
CCPP/MH20	80	-	-	20
CCPP/MH30	70	-	-	30
CCPP/EXOLIT20	80	-	20	-
CCPP/EXOLIT25	75	-	25	-
TPP	-	100	-	-
TPP/MH20	-	80	-	20
TPP/MH30	-	70	-	30
TPP/EXOLIT20	-	80	20	-
TPP/EXOLIT25	-	75	25	-

Table 1. Formulation of FR composites

3. Characterization techniques

3.1 Fire tests

Combustion test was performed on a Fire Testing Technology Cone calorimeter according to ISO-5660-1 standard procedure. The bottom and the sides of each specimen, prepared by compression moulding in a laboratory press equipped with heating plates (GiBitre Instruments) at 190 ^{o}C, was wrapped in an aluminum foil and exposed horizontally to an external heat flux of 35 kW/m^2. For each composition, a total of three specimens were tested. The dimension of specimens was 50 × 50 × 3 mm.

Limiting oxygen index (LOI) test was performed on a Fire Testing Laboratories instrument according to the standard Oxygen Index Test UNI EN ISO 4589-2. LOI values describe a procedure for measuring the minimum concentration of oxygen in an oxygen/nitrogen atmosphere that will just sustain combustion in a candle-like configuration of a top-ignited vertical test specimen. The dimension of the specimens used for this test was 75 x 5 x 3 mm.

UL 94 horizontal burning test was carried out according to D 635-98 standard procedure.

For each composition, a total of three specimens were tested and the average was calculated. The dimension of specimens was 125 x 12 x 3 mm.

3.2 Thermal analysis

The samples were analyzed by thermogravimetric analysis (TGA) using a Q 500 Thermal Analyzer under both nitrogen and air flow from 50 ^{o}C to 800 ^{o}C at a heating rate of 10^{o}C/min.

3.3 Morphological characterization

Scanning Electron Microscopy (SEM) micrographs were obtained by using a LEO 1450 VP instrument. EDS elemental analysis was performed with an INCA Energy Oxford probe and the data were recorded with INCA software. The samples were prepared by cryogenic fracture in liquid nitrogen (to avoid plastic deformation) and then gold sputter-coated.

3.4 Mechanical measurements

Tensile properties were measured by a Zwick Roell Z/010 dynamometer at a cross-head speed of 50 mm/min. The tensile bars were prepared by injection molding press according to UNI EN ISO 527-2.

4. Results and Discussion

In Table 2 are reported the main parameters from cone calorimeter measurements on the samples, in particular time to ignition (TTI), peak of heat release rate (pkHRR), Specific Extension Area (SEA) and total smoke released (TSR). The MH-containing composites showed a time to ignition higher with respect to the polymer matrices (Table 2). The increase in time to ignition of the CCPP/MH composites may be due to the endothermic decomposition of MH. Moreover the MH-containing composites have shown a significant reduction of HRR value with respect to the CCPP matrix: slower combustion is evidenced by the lower HRR peak (pkHRR, -37% and -48%, respectively). In the case of the use of Exolit flame retardant there is no effect on CCPP matrix and only a slight decreas of the peak in the case of TPP matrix. Similar to the HRR and THR curves, the MH-containing composites showed significant reduction of the values of the above the smoke parameters (SEA and TSR) mainly in the case of CCPP matrix. As it is known, MH acts as flame retardant due to its endothermic decompositions with the formation of water vapor and metal oxide residue ($Mg(OH)2 \rightarrow MgO+H2O$ (1300 kJ/Kg)[1]. Thus, these results may be attributed due to the stable-solid char formation which can suppress the release of smoke.

	TTI	**pkHRR**	**SEA**	**TSR**
	(s)	($kW \cdot m^{-2}$)	(m^2/kg)	($m^2 \cdot m^{-2}$)
CCPP	60±6	324±32	490±49	1203±120
CCPP/MH20	63±6	204±20	129±13	302±30
CCPP/MH30	74±7	167±17	192±19	571±57
CCPP/EXOLIT20	38±4	319±32	261±26	629±63
CCPP/EXOLIT25	34±3	328±33	251±25	563±56
TPP	62±2	520±60	632±18	1429±35
TPP/MH20	78±4	389±26	446±37	1073±83
TPP/MH30	77±2	345±11	441±22	1049±60
TPP/EXOLIT20	44±1	391±5	431±24	1110±87
TPP/EXOLIT25	49±2	383±16	368±17	846±2

Table 2. Main parameters from cone calorimeter

The influence of MH and Exolit flame retardants on the flame retardancy of the polypropylene filled with calcium carbonated and talc matrices is shown in Table 3. It can be seen that the both CCPP and TPP matrices containing MH showed an significant increase of LOI value. On the other hand the effect of Exolit in this parameter is negligible.

Sample cod	**Limiting oxygen index**
	(vol.-%)
CCPP	20.5
CCPP/MH20	24.2
CCPP/MH30	25.3
CCPP/EXOLIT20	21.0
CCPP/EXOLIT25	21.2
TPP	21.9
TPP/MH20	23.2
TPP/MH30	23.6
TPP/EXOLIT20	21.1
TPP/EXOLIT25	21.7

Table 3. Limiting oxygen index (LOI) of the samples

On the most interesting material, after the flame test results, CCPP/MH20 thermal analysis and mechanical properties are performed.

Thermogravimetric analysis can be a useful technique not only to describe thermal decomposition process, material stability, and effects of additives on a material's thermal performance, but also the flammability behavior [2,3]. Therefore, to investigate the effects of MH filler on polypropylene filled with calcium carbonate, the thermal degradation behavior and the mass of the residue obtained under both inert and oxidative atmospheres were compared.

It was observed that the maximum weight loss rate temperature (Tmax) of the CCPP/MH20 composite is almost within the same temperature range of the CCPP matrix for analysis performed under nitrogen atmosphere (Table 4). These results show that MH did not affect the degradation mechanism of the CCPP matrix under the employed conditions. However, concerning the onset decomposition, it was observed a decrease which can be due to water elimination from MH decomposition [4].

The decomposition of the CCPP/MH composites was quite different under oxidative atmosphere. The CCPP matrix diminished its temperature of decomposition to about 369 °C, while this temperature in the CCPP/MH composites was 400 °C and 407 °C, respectively (Table 4). However, both the matrix and the composites decompose at lower temperature toward to the decomposition under inert atmosphere which took place at higher temperature.
The delay of thermal decomposition of the CCPP/MH composites under oxidative atmosphere, it may be explained by the proposed mechanism of the MH flame retardant: as water is released, a magnesium oxide protective layer forms, preventing oxygen contact with the polymer matrix.
Flame resistance can also be evaluated from the residue after pyrolysis of the materials. Increasing residue formation can lead to a enhancing of flame retardancy because it can hold up the release of the volatile degradation gases from the sample, slows down the heat flow to the sample and reduce the oxygen diffusion into the material [5]. The amount of the residue left after degradation at 800 oC of the CCPP matrix was only 21 wt.-%, while the residue left of the CCPP/MH composite was much higher (35 wt.-%).

Sample cod	**a)T_{onset}**	**b)T_{max}**	**Residue**	**T_{onset}**	**T_{max}**	**Residue**
	(°C) air	**(°C) air**	**(%) 800°C**	**(°C) N_2**	**(°C) N_2**	**(%) 800°C**
CCPP	288	369	21	417	468	21
CCPP/MH20	355	407	35	413	467	35

Table 4. TGA analysis of CCPP matrix and CCPP/MH20 composite. a)T_{onset}: the onset of decomposition temperature (temperature at 5% weight loss); b)T_{max}: maximum weight loss rate temperature.

SEM micrographs of the CCPP/MH20 composite revealed the existence of aggregates being distributed all over the matrix (Figure 1). The light areas reflect the Ca and Mg elements, while the dark area show PP. Furthermore, the EDS mapping confirmed the presence of calcium in aggregate form (green spot), whereas magnesium look quite uniform distributed within the composite suggesting a homogenous dispersion of the flame retardant.
Take into consideration that the strength of two-phase composite materials depends on effective stress transfer between filler and matrix, to get a high strength composite a strong interfacial bonding between particles and polymer matrix is required. Fu et al. [6] reported that mechanical properties of particulate-polymer composites are influenced by the particle size, particle/matrix interface adhesion and particle loading.
From SEM micrographs it can be seen clearly that the interfacial adhesion filler/matrix is poor and this aspect affect the strength of the CCPP/MH20 composite.
As it can be seen from Table 5 the incorporation of MH filler into the CCPP matrix increased the Young's modulus, by ca. 20 %, which can be attributed to the inherent rigidity of MH particles. A reduction up to 10% in both parameters, tensile strength and elongation at break, was observed due to the poor interfacial adhesion between the CCPP matrix and MH filler.

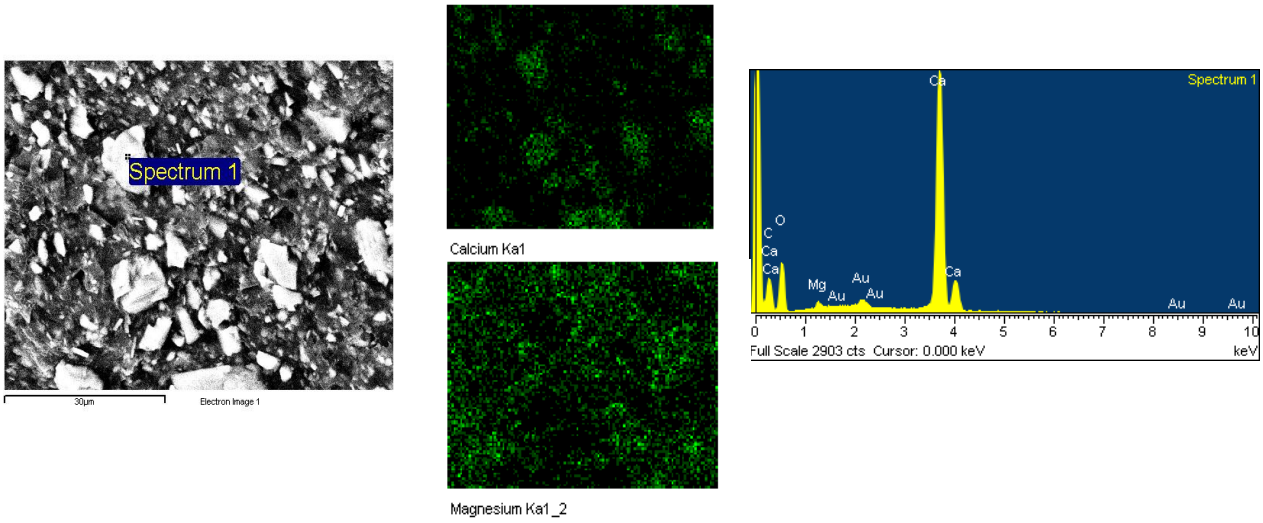

Figure 1. SEM micrographs and EDS mapping of the CCPP/MH20 composite

Sample cod	Young's modulus	Tensile strength	Elongation at break
	(MPa)	(MPa)	%
CCPP	2085	17.5	264
CCPP/MH20	2534	15.6	236

Table 5. Mechanical properties of the CCPP matrix and CCPP/MH20 composite.

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