Halogen Free Flame Retardant Agents for Polypropylene in Wire Coating Process

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Summary: the processing behaviour and physical properties of polypropylene/flame retardant blends were investigated in order to evaluate their use in the wire-coating process. In particular, the need of flame retardancy, suitable melt processability and good mechanical properties of blends was taken into account. Three types of halogen free flame retardants were chosen and were melt blended to the polypropylene matrix. Blends properties were analysed by rheological, mechanical, and thermal characterization including flame retardancy tests. The wire coating process was also performed by a laboratory wire coating apparatus. The results demonstrated that some of the blends are suitable for the purpose of flame retardancy of electrical household wires as an alternative to PVC.

Keywords: blending; flame retardance; poly(propylene)(PP); processability; wire coating

Introduction

Polymeric materials are used in many areas under ever more demanding "environmental friendly" approaches. This is the case of electrical insulation of conductive wires which is performed usually by making use of various thermoplastic polymers which are well known fire hazardous materials. Hence, in order to reduce the combustion risk related to their employment in household applications, the use of flame retardant agents (FR's) represents an imperative. FR's are the most important family of polymers additives being usually present at loadings ranging between 10 and 30% in the final plastic composition. As far as electrical cables insulation is concerned, polyvinylchloride (PVC) is one of the most used thermoplastic material due to its intrinsic low rate of combustion, high resistance to ignition and flame propagation, low cost, ease of processing and good mechanical properties. Nevertheless, PVC also presents problems related to the high toxicity of the gases produced during the combustion. Substitution of PVC matrix with other low cost and recyclables resins like polyolefines (PP, PE) seems to be thus interesting. Unluckily, these thermoplastics display higher flammability and therefore need high rates of flame retardant fillers to improve the non-combustion properties. The most effective flame retardants used thus far are halogens, phosphorus, antimony, and heavy-metal based compounds,[1–3] which have a strong environmental impact and high toxicity. Thus, the development of new flame retardant materials has been driven to halogen free intumescent flame retardants. The action mechanism of intumescent flame retardant additives[4–6] is related to their promotion of carbon foam production on polymer surface when the thermoplastic material is exposed to flame. The carbon foam layer, which builds up during combustion, protects the polymer through heat-insulating effect, and reduction of further oxygen access.

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In the present work blends of PP and intumescent flame retardant agents were analysed.

In particular, three kinds of halogen free flame retardants were tested at different loadings and processing conditions. Rheological, processability behaviour of blends were assessed and properties, such as mechanical and flame retarding effect, were evaluated.

Materials and Methods

The matrix used in the present work is a commercial polypropylene (PP) (HiFax CA10A), supplied by Basell polyolefines. Its main physical characteristics are: MFI (230 °C, 2.16Kg) of 0.6g/10′, density of 0.880 g/cm^3, melting point of 142 °C.

The flame retardant additives were chosen among some commercial intumescent fillers, which inhibit propagation of flame by forming a carbon layer on the polymer surface during combustion. In particular three powders were used:

1) Budit 3076 DCD supplied by Budenheim Ibérica, (Budit);
2) Exolit AP 750 supplied by Clariant, (Exolit);
3) DG/HF 2000 supplied by De Grandi s.r.l., (DGHF).

In order to prevent polypropylene degradation during processing, 0.1%wt of Irganox 1010 and 0.1%wt of Irgafos 1016, supplied by Ciba Specialty Chemicals, were used.

Blends of fillers and polypropylene were prepared by melt compounding in a co-rotating twin-screw extruder, HAAKE Rheocord 9000, D = 20 mm (L/D 20).

Extrusion tests were conducted in order to evaluate process parameters for the production of pelletized compound to be used for further investigations and for wire-coating process. In particular the evaluation of flame retarding behaviour and the mechanical characterization were conducted on samples cut from extruded ribbons with a thickness of 2 mm).

Blends were produced with amount of flame retardant of 15, 20, 25 and 30% wt/wt. The temperature profile of the extruder (four zones) was maintained at 160 °C, 180 °C, 200 °C, 200 °C from hopper to die; the screw speed was maintained at 60 rpm.

SEM micrographs of compounds were realized by a Leica Stereoscan 440 scanning electron microscopy. The specimens, fractured in liquid nitrogen, were previously coated with a conductive layer.

Flame retarding behaviour was investigated using the UL-94 test (ASTM D3801-00) to evaluate the degree of the flame spread of specimen under given burning conditions. In particular, this kind of test is used to provide an indication of a material's ability to extinguish an ignited flame on a vertical specimen.

The UL 94 rating categories used for the present work are summarized as follows:

V-0 = burning stops within 10 seconds; no drops allowed
V-1 = burning stops within 30 seconds; no drops allowed
V-2 = burning stops within 30 seconds; drops of flaming particles are allowed

For each test at least five samples were used. Neat polypropylene had no flame retardancy and was not classified. This is also verified by TGA analysis which shows that char yield of polypropylene is almost zero.

The rheological behaviour of compounds was studied both at low and high shear rates.

Rheological measurements at low shear rate were executed using a strain controlled rotational rheometer (ARES Reometric Scientific) with parallel plates configuration with a starting gap of 0.5 mm in a nitrogen environment. To allow normal stresses relaxation, a variable delay was imposed before testing.

For rheological measurements at high shear rate a capillary rheometer (ACER

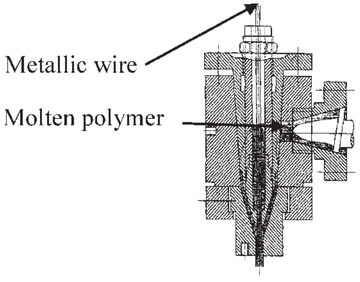

Figure 1.
Section of die used for the wire coating process.

Reometric Scientific) was used with capillary L/D ranging from 10 to 40. Most of rheological analyses were performed at 200 °C, although measurements were conducted over the range 200–220 –240 °C.

Blends processability was assessed by the evaluation of the behaviour during the extrusion process. In particular melt pressure, torque and extrudate appearance were taken into account. The same assessments were made during the wire coating process which was conducted using the pelletised strand coming from previous compounding process, with the same extruder Haake Rheocord 9000; the wire coating die is sketched in Figure 1. The final die diameter is of 2 mm and wire diameter used for the coating process was 1 mm.

During wire coating extrusion process the temperature profile of the extruder was maintained at 170 °C, 180 °C, 200 °C, 200 °C (from hopper to die), and screw speed of 60 rpm. The take up of wire was performed at a speed of 70 mm/s.

Mechanical tensile properties of polypropylene and its composites were measured according to ASTM D638-99 using an Instron 4204 system tensile tester at the crosshead speed of 1.7 mm/s (100 mm/min). Specimens for tensile testing were prepared by extrusion of strips which were then cut at room temperature according to the ASTM D638.

Results and Discussion

Rheological Characterization

The knowledge of flow behaviour is essential for any kind of melt processing of a thermoplastic polymer. The case presented in this work is a typical two phase system in which the flame retardant acts as a solid filler in the molten thermoplastic matrix. The difficulties rising in such systems are related both to filler dispersion and rheological instability during the extrusion process which can induce extrudate defects. Rheological measurements are therefore used in order to highlight the differences of flow properties between the pristine matrix and the two phase systems. The rheological results are reported for blends of PP with 25% (wt/wt) of flame retardant agents, which allowed V-0 flame retardance rating as shown later. Viscosity curves at 200 °C, are reported in Figure 2. The curves reveal a shear thinning

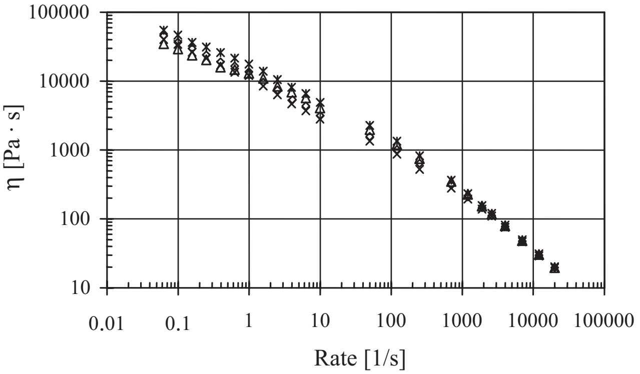

Figure 2.
Rheological curves of PP/25% wt/wt FR's blends at 200 °C; △ = PP, × = PP/Budit, ◇ PP/Exolit, ✱ = PP/DGHF.

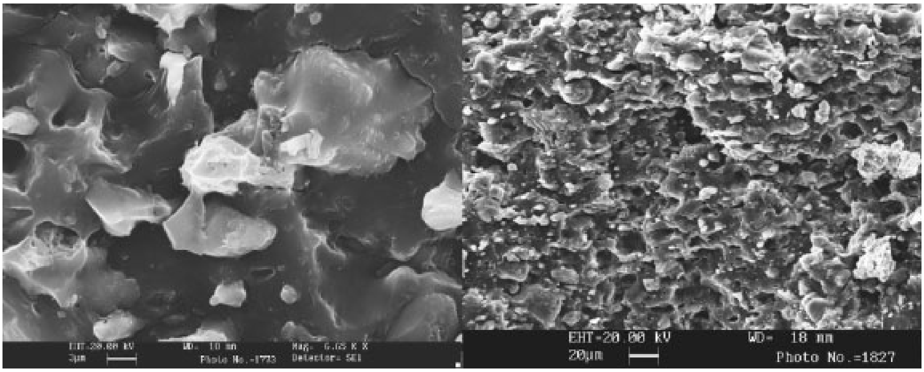

Figure 3.
SEM images of the blend PP/25% Exolit.

behaviour with flow curves converging at high shear rates for all systems while negligible differences in viscosity are present in the low frequency region. Of course, the pristine PP matrix shows a lower viscosity through the whole range of frequency/shear rates.

Scanning Electron Microscopy

The dispersion of powders in polypropylene matrix is evidenced in Figures 3–5 where SEM images are reported for the three blends prepared by extrusion with a content of 25% by weight of flame retardants. In particular Exolit and Budit show a slight smaller size distribution respect to DGHF. However, the comparison of SEM images at small magnification does not allow the evaluation of different grade of dispersion of the additives.

Processability

The process of wire coating involves the extrusion of the molten polymer through an annular die around a metallic wire which is simultaneously pulled through the die itself (Figure 1). Once the wire has been accurately centred in the die, the polymeric film thickness can be adjusted by tuning the extruder screw speed (which in turn governs the melt pressure and flow rate through the die) and wire take up speed. Besides a correct set up of the operation, the main problem which can raise during the process, particularly in the case of filled polymers, is a not uniform coating of the

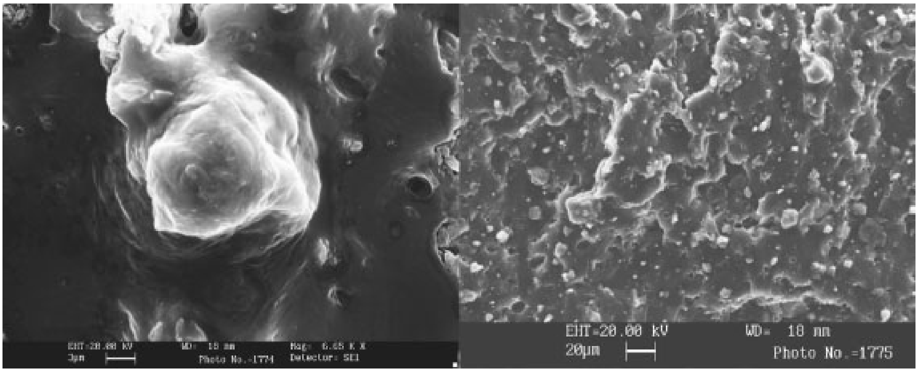

Figure 4.
SEM images of the blend PP/25% Budit.

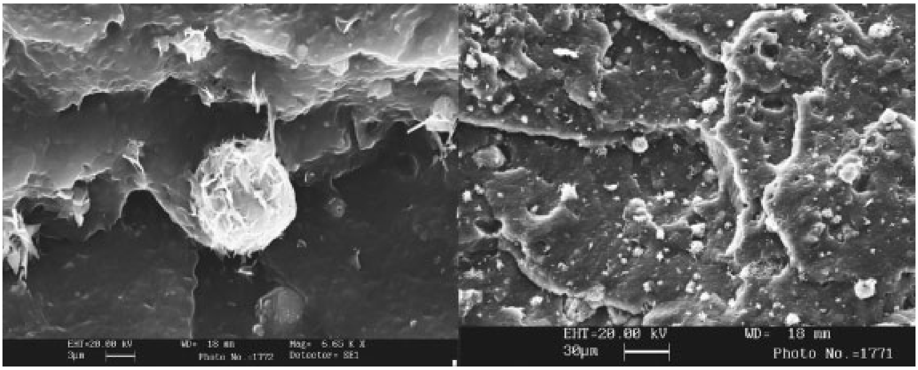

Figure 5.
SEM images of the blend PP/25% DGHF.

wire. In our case, the dispersion of flame retardant powders in the polypropylene was considered and attention was focused on blends at higher additive content (25% wt/wt).

A single step process of compounding and wire coating extrusion failed. The output flow of extruder did not result regular enough for the operation of wire coating and the extrudate surface was very rough. A two steps operation was thus performed: first polymer and flame retardant compounding and granulation was accomplished by the twin screw extruder and a strand pelletizer; then the pelletized compound was used for wire coating extrusion. This process was performed successfully with very similar behaviour of all the blends analysed.

During the twin screw compounding, torque, die pressure and output flow rate were measured during the process. These parameters are reported in Table 1 for blends with 25% wt/wt of flame retardant.

The process apparatus used for the present study allowed a sufficient filler dispersion in the PP matrix for all the samples and only slight differences were tested both in process parameters and blends morphology. As shown in Table 1, there is an increase of torque, pressure and output flow rate of blends respect to PP alone. Actually, such a result was expected since the small differences of melt viscosity, as stated in Figure 2. Moreover blends parameters slightly differ each other probably due to little granulometric difference of fillers.

Flammability Tests

Specimens of the compounds for the flammability tests were cut in the appropriate shape and dimensions from extruded strips. According to UL-94 test procedure, the results are given in terms of flammability classes. Ratings are classified as V-0, V-1, V-2 ordered by increasing flammability. A class of flammability V-0 is requested for wire coating materials.

The flame retardants used for the present work were almost able to retard or, in some cases, even to completely suppress polymer combustion.

Table 1.
Extrusion data of PP and blends during compounding at screw speed of 60 rpm.

Material	Torque [N × M]	Head Pressure [BAR]	Output [G/MIN]
Polypropylene (PP)	17 ± 2	16 ± 2	12 ± 1
PP/Exolit 25%	19 ± 2	20 ± 2	19 ± 1
PP/Budit 25%	18 ± 3	18 ± 1	16 ± 2
PP/DGHF 25%	20 ± 2	19 ± 2	18 ± 1

Table 2.
Results of flammability tests.

Material	Classification
PP + 15% DGHF	n.c.
PP + 20% DGHF	V-2
PP + 25% DGHF	V-0
PP + 30% DGHF	V-0
PP + 15% Budit	n.c.
PP + 20% Budit	V-2
PP + 25% Budit	V-0
PP + 30% Budit	V-0
PP + 15% Exolit	n.c.
PP + 20% Exolit	V-0
PP + 25% Exolit	V-0
PP + 30% Exolit	V-0

The polypropylene without flame retardant continued burning for a long time and it was thus rated as not classified (n.c.). The compounds show drastically reduced burning time. In some cases burning drops were produced during the test. The results of the UL-94 test executed on the blends are reported in Table 2. Of course the increase of the amount of flame retardant leads to a decrease of burning time. It can be seen that a load of 25% of flame retardant assures the V-0 rating of flammability for all three fillers. Lower amounts (15–20%) are not enough to suppress the flame except the case of blends based on Exolit AP 750, which presented shorter burning times classified as V-0 rating with a content of 20%.

Mechanical Properties

Mechanical tensile properties were evaluated for blends with a FR content varying from 15 to 30%. The results are reported in terms of tensile modulus, elongation at break and stress at break in function of filler contents and are shown in Figures 6, 7 and 8 respectively. As expected, the effect of the intumescent powders on tensile performances resulted in an increase of elastic modulus and decrease of ultimate properties. In particular the increase of filler content negatively affects the elongation at break although quite high values are exhibited as shown in Figure 7. On the other hand, an increase in values of stress at break was detected for the blends with a filler content up to 20%.

Conclusions

In the present work the effectiveness of some commercial flame retardant fillers performance within a polymeric matrix was evaluated. The assessment was performed on some technological properties with a particular regard to the processability and flame retarding behaviour of blends with an amount of filler varying up to 30% by weight.

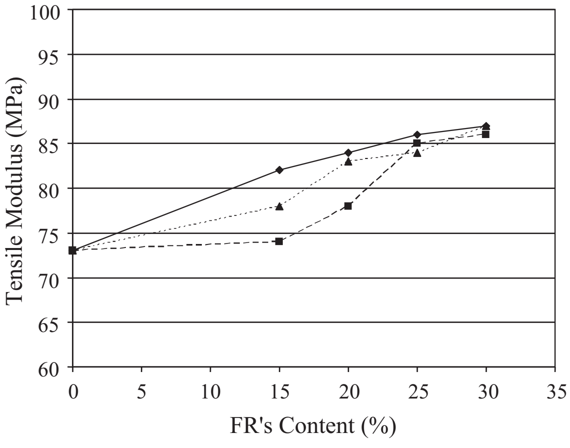

Figure 6.
Tensile modulus of blends vs. FR's content; ◆ = Budit, ■ = Exolit, ▲ = DGHF.

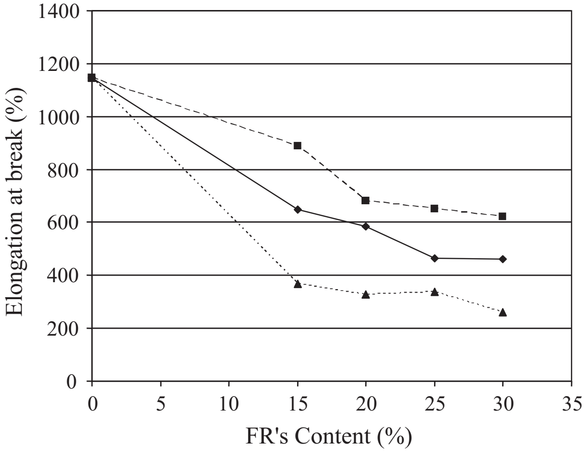

Figure 7.
Elongation at break of blends vs. FR's content; ◆ = Budit, ■ = Exolit, ▲ = DGHF.

It was shown that the introduction of filler brings flame retarding benefits, with only some slight negative influence on physical-mechanical properties. In particular, the compounds displayed a viscosity increase respect to the PP matrix as measured by rheological tests. Nevertheless the shear thinning behaviour of blends keeps at reasonable values the viscosity at the shear rates involved during the extrusion and wire coating processes. This fact can be regarded as a positive result in terms of processability of the blends. Moreover, the dispersion of the fillers remains a crucial operation. Probably the little differences in the optimum flame retardant content can be recognized as a consequence of the morphology resulting from processing conditions used in the work. However the 25% wt content assures the V-0 flame retarding class for all three fillers. As far as mechanical performances are concerned, although some negative effect was tested in particular for elongation at break

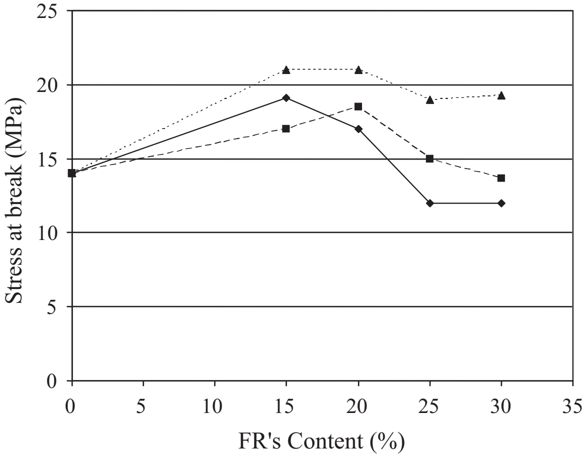

Figure 8.
Tensile stress at break of blends vs. FR's content; ◆ Budit, ■ = Exolit, ▲ = DGHF.

(decreased) and the tensile modulus (increased), they do not vary considerably respect the matrix failure properties.

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