Reprocessed High Impact Polypropylene Containing Oil Pollutant Exhibiting Flame Retardant Properties

Mathilde Casetta,[*1,2,3,4] *Damien Delaval,*[1,2,3,4] *Michel Traisnel,*[1,2,3,4]
Serge Bourbigot[1,2,3,4]

Summary: In this work, the reaction to fire of reprocessed polypropylene (PP)/ Ethylene Propylene Rubber (EPR) materials containing engine oil as pollutant was investigated by mass loss calorimetry. It was compared to the behaviour of the corresponding original high impact PP material. In order to flame retard the polymers, an intumescent system was studied in combination with zinc borate (ZB) as potential synergistic agent. It is shown that 20% of additives are necessary to obtain good FR properties. The use of ZB greatly improves the reaction to fire of original PP/EPR materials due to the formation of borophosphates during the degradation process that permit to reinforce the char structure. In the case of the polluted and reprocessed formulations, ZB has no influence on the fire performance because the minerals included in the engine oil act also as a flame retardant. For the two types of materials, it is demonstrated that the expansion rate at the beginning of the intumescent process plays a crucial role in the formation of an efficient insulating layer at the surface of the substrate. On the contrary, the fire performance is not related to the thickness of the carbonaceous shield.

Keywords: engine oil; flame retardance; intumescence; polypropylene; reprocessing

Introduction

In Europe, the treatment of end-of-life vehicles (ELV) is a major environmental concern. According to the Directive 2000/53/EC, the automotive industry will have to meet recycling targets of 95%, by an average weight per vehicle and year for all ELV, by January 2015.[1] The main problem lies in the recycling of plastics materials which are increasingly being used in the automotive field due to their numerous properties[2–3] and among these plastics, polypropylene (PP) comprises the largest fraction. Many times, uses of PP in some of the automotive parts require enhanced toughness, such as in the cases of door panels, bumpers, and battery cases.[4] This can be achieved by blending PP with elastomers like ethylene propylene rubber (EPR) and ethylene propylene diene monomer (EPDM), creating a composite known as high-impact PP. Such PP/EPR blends are complex materials formed by a matrix of isotactic polypropylene in which the poly(ethylene-propylene) elastomeric copolymer (EPR) is finely dispersed.[5] This makes these different polymers difficult to separate and recover at the end of a vehicle's life, especially because they are also often polluted by liquids such as engine oil, coolant... Thus the direct recycling has to be considered and many applications can be expected for these materials, especially in building, transport or for electric devices. But these applications require a degree of flame retardancy (FR) and PP-based materials are highly flammable.

The aim of this study is to improve the flame retardant properties of reprocessed

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[1] Univ Lille Nord de France, F-5900 Lille, France
E-mail: Mathilde.Casetta@univ-lille1.fr
[2] ENSCL, PERF-LSPES, F-59652 Villeneuve d'Ascq, France
[3] USTL, PERF-LSPES, F-59655 Villeneuve d'Ascq, France
[4] CNRS, UMR8008, F-59652 Villeneuve d'Ascq, France

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PP/EPR materials polluted with engine oil (EO) to obtain high added value products. Previous study[6] has shown that the thermal stability and the reaction to fire of PP/EPR were increased in the presence of EO. One of the promising approaches to increase the flame retardancy while preserving the mechanical properties is to apply intumescent fire retardant (FR) additives. Upon heating, these additives form a foamed cellular charred layer on the surface of the product, which slows down the heat and mass transfer between the gas and the condensed phase.[7] Ammonium polyphosphate (APP) is a very commonly used flame retardant in PP, often combined with other species in order to obtain synergism.[8] APP can also be found in intumescent systems used to flame retard EPR.[9] In our work, an intrinsic intumescent system based on APP was incorporated in the different PP/EPR materials in combination with zinc borate (ZB) because Fontaine et al.[10] demonstrated that ZB acts as a synergistic agent in FR PP formulations. Then, the FR properties have been evaluated by mass loss calorimetry. The determination of physical parameters linked to the intumescent process has been done via a new experimental setup to try to explain the differences obtained between original materials and polluted/reprocessed ones in terms of fire performance.

Experimental Part

Materials

To better understand the influence of oil pollution and reprocessing on the fire properties, model materials were produced, using commercially available products. The high impact PP was supplied by SABIC and is made of a polypropylene matrix (78 wt.-%) containing an EPR (about 50% of ethylene) (22 wt.-%) phase. Concerning the pollutant used in the materials, Total Activa 7000 10W40 engine oil (EO) was purchased. To determine the mineral elements in this commercial oil, electron microprobe analyses were realized. First, the engine oil was put in a furnace and heated up to 800°C at 10°C/min. The residues were then washed, dried and finally analyzed. The electron probe microanalyzer (EPMA) using wavelength dispersive X–ray spectrometers was used to perform element analysis. The microanalytical work was carried out on a Cameca SX-100 microprobe analyzer at 20 kV 20 nA. Several crystals were used to detect a large range of chemical elements: LIF, PET, TAP and PC2. The X-ray spectrograms allowed to detect the presence of phosphorus, magnesium, zinc, calcium and sulphur.

Then, to make the intumescent formulations, a commercial ammonium polyphosphate (APP) derivative (trade name Exolit AP765) supplied by Clariant and consisting of a blended mixture of APP ($(NH_4)_n + 2P_nO_{3n+1}$) and tris-(2-hydroxyethyl)isocyanurate (THEIC) was used. This intrinsic intumescent system may be used with a wide range of thermoplastics, especially polypropylene blends. A commercial grade of zinc borate (ZB) supplied by Rio Tinto Minerals was selected to study the potential synergistic effects between the different components of the intumescent formulations.[11] *Firebrake* ZB is a multifunctional boron-based fire retardant, composed of 48% B_2O_3, 37.5% ZnO and 14.5%H_2O. The median particle size is around 8 microns. The seven formulations listed in Table 1 have been tested with the original PP/EPR first and then with the polluted and reprocessed PP/EPR (written Reprocessed PP/EPR/EO).

Table 1.
Composition of the different formulations.

	PP/EPR (78/22) (wt %)	APP (wt %)	ZB (wt %)
PP/EPR	100	0	0
PP/EPR 10%APP	90	10	0
PP/EPR 9%APP 1%ZB	90	9	1
PP/EPR 8%APP 2%ZB	90	8	2
PP/EPR 20%APP	80	20	0
PP/EPR 19%APP 1%ZB	80	19	1
PP/EPR 18%APP 1%ZB	80	18	2

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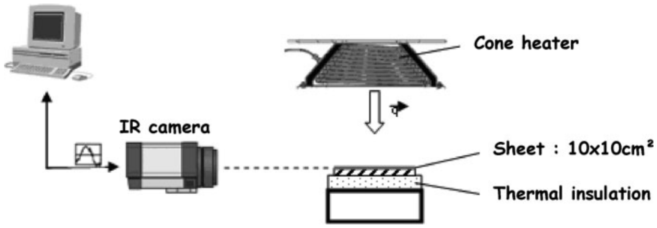

Figure 1.
Experimental set-up for measuring the swelling during a mass loss calorimeter experiment using infrared camera.

Processing

The successive extrusion runs were carried out on a co-rotating twin-screw extruder (Clextral BC 21). To simulate the contamination of the samples, 2 wt.-% of EO was incorporated in mass during extrusion and the mixtures underwent 6 successive cycles of extrusion to simulate recycling. The experimental conditions were described in a previous paper which also explains the choice of the number of reprocessing cycles.[6] Granulates were then injected at 230°C into an injection molding machine Billion Visumat 1000 to realize 300x100x3 mm^3 sheets. The FR materials were prepared by melt mixing at 190°C in a Brabender internal mixer with a rotor speed of 50 rpm for 12 minutes. Sheets ($100 \times 100 \times 3 mm^3$) were obtained by compression moulding (Darragon press) under a pressure of 10 kN for 3 minutes and then 40 kN for 5 minutes.

Fire Testing

FTT (Fire Testing Technology) Mass Loss Calorimeter was used to carry out measurements on samples following the procedure defined in ASTM E 906. The equipment is identical to that used in oxygen consumption cone calorimetry (ASTM E-1354-90), except that a thermopile in the chimney is used to obtain the rate of heat release (HRR) rather than employing the oxygen consumption principle. Our procedure involved exposing specimens measuring 100 x 100 x 3 mm^3 in horizontal orientation. External heat flux of 35 kW/m^2 was used for running the experiments. This flux corresponds to common heat flux in mild fire scenario. When measured at 35 kW/m^2, HRR is reproducible to within ±10%. The data reported in this paper are the average of three replicated experiments.

Swelling

An experimental set-up was designed to shoot a mass loss calorimeter experiment using an infrared camera (Figure 1). The advantage of infrared camera is to get clear images to make image analysis. This technique, used in dynamic conditions (from a movie), allows the measurement and quantification of char swelling. In this approach, it is assumed that the expansion is homogeneous and occurs in one dimension. The benefit is thus to get a quantitative evaluation of the sample thickness as a function of time during the formation of the intumescent structure. This way, the swelling speed of the char can be determined, recognizing that this factor has an influence on the efficiency of the protective layer formed. With this technique, results are reproducible to within ±5%.

Results and Discussion

Reaction to Fire

Non reprocessed and Non Polluted Materials

Figure 2 gives HRR values as a function of time for the different formulations containing only the original PP/EPR. HRR curve of the initial material is in the form of a single peak exhibiting a maximum of 448 kW/m^2. The addition of 10% of APP induces a sharp decrease in the peak of

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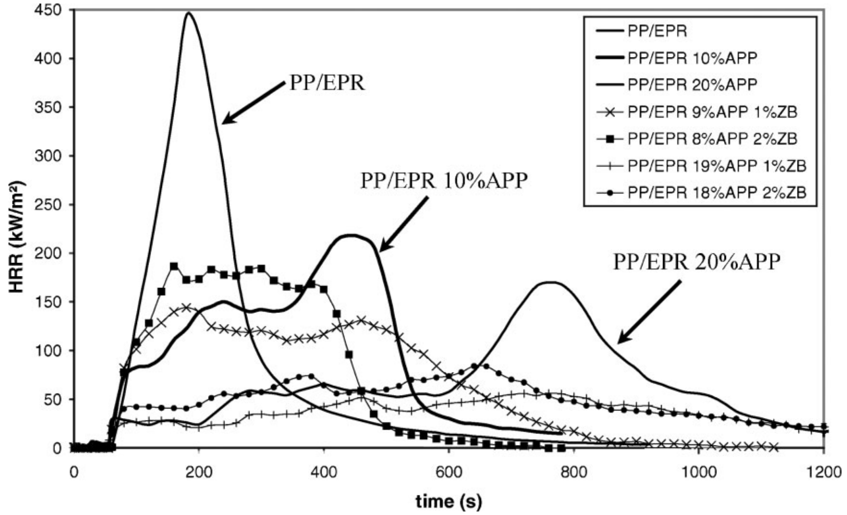

Figure 2.
Heat release rate (HRR) as a function of time of the different PP/EPR intumescent formulations.

HRR (pHRR) value which is roughly divided by 2 (220 kw/m^2). This phenomenon is due to the formation of a charred layer at the surface of the material and this is confirmed by the shape of the HRR curve, exhibiting two peaks and typical of intumescent systems.[12] The first peak is assigned to the ignition and to the flame spread on the surface of the material and then, when the HRR values become constant, to the protection by the intumescent coating. The second peak is explained by the partial destruction of the intumescent structure (formation of cracks and holes at the surface of the intumescent coating) and the formation of a carbonaceous residue.[13]

Then, the substitution of 1% of APP by ZB (9%APP/1%ZB sample) leads to a further decrease of the pHRR but of a lesser extent (maximum value of 145 kW/m^2). The main difference in HRR curves of 10%APP and 9%APP/1%ZB samples is the decrease of heat released for the second peak when ZB is present. At the same time, the formation of the intumescent structure (first peak) seems slightly faster. So it can be assumed that the degradation of the 9%APP/1%ZB material is less significant because it is protected more rapidly and thus the quantity of heat released is inferior when the char is destroyed. Now, if the 8%APP/2%ZB sample is considered, the opposite trend is observed because the pHRR value (191 kW/m^2) is close to that of the 10%APP material. Moreover, the destruction of the sample containing 2%ZB is faster than for the two formulations mentioned previously and the two steps corresponding to intumescent systems are not clearly visible in that case.

Regarding the 20%APP sample, the pHRR value is 174 kW/m^2, slightly lower than with 10%APP and concerning the shape of the HRR curve, the second peak appears much later than with 10%APP which means that the degradation of the char is strongly delayed. The addition of ZB in the blends containing 20% of additives leads to a strong reduction of the HRR maximum whatever the quantity of ZB. Moreover, the pHRR value for the sample containing 2%ZB (86 kW/m^2) is slightly superior to the 1%ZB (56 kW/m^2). Therefore the comparison between all the intumescent formulations shows that the best results are obtained with the 19%APP/1%ZB formulation because in that case the

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presence of 1%ZB allows to obtain a strong synergistic effect and thus better FR properties.

These results agree with previous works which showed that ZB was an efficient synergistic agent in different combinations of FR polymeric materials.[14] Wu and al.[15] have shown that the addition of 3% ZB in a LDPE/12%APP/8%PER material results in an improvement of fire performance because of the excellent quality of the char formed. Bourbigot and al.[16] have proved that this more effective char decreases the degradation rate of the polymer and as a consequence, decreases HRR values in comparison with formulations without ZB. More precise investigations on the role and mechanism of action of boric acid and coated APP used as flame retardants have demonstrated that a reaction between the degradation products of boric acid and coated APP took place, leading to the formation of borophosphate.[17] In this way they have suggested that the formation of borophosphate was responsible for the development of a hard and mechanically resistant char. So it can be assumed that in our formulations, the same type of reaction between the degradation products of APP and ZB takes place thus reinforcing the char structure and improving the FR properties for the 19%APP/1%ZB system.

Reprocessed PP/EPR/EO Materials

HRR curves of the intumescent formulations containing reprocessed PP/EPR/EO are shown Figure 3. The shape of these curves is similar to the corresponding ones obtained for the original PP/EPR systems but there are major differences in the pHRR values. The changes are already marked for the reprocessed PP/EPR/EO sample which possesses a pHRR value of 280 kW/m^2 against 448 kw/m^2 for the PP/EPR material that is a 37% decrease without adding any intumescent additive. This phenomenon can be explained by the presence of mineral additives such as phosphorus, magnesium, zinc, calcium and sulphur in the commercial EO detected by electron microprobe. But many phosphorous and magnesium based products are efficient as FR additives. So the presence of such elements in the EO might stabilize the polymeric matrix and improve the reaction to fire of the reprocessed PP/EPR/EO sample. The incorporation of APP induces a strong reduction of the pHRR values: 49% and 77% decrease

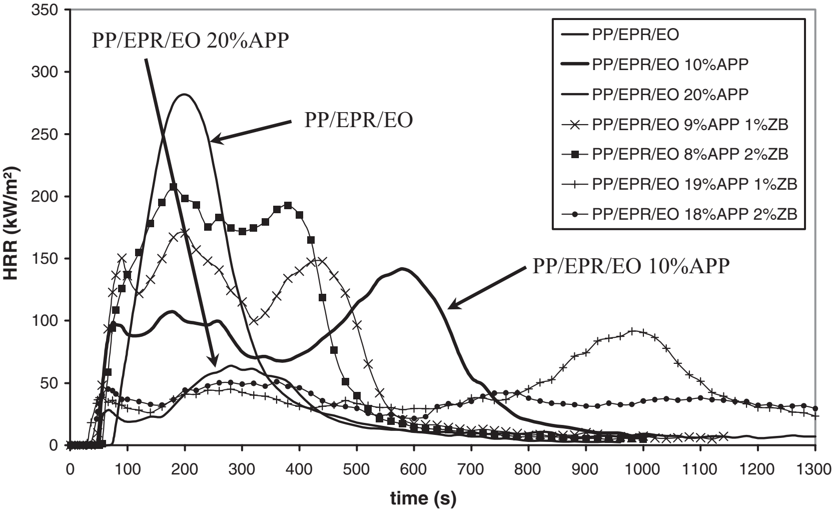

Figure 3.
Heat release rate (HRR) as a function of time of the different reprocessed PP/EPR/EO intumescent formulations.

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respectively for the 10%APP and 20%APP formulations. The substitution of APP by ZB for the formulations containing 10% of additives leads to a degradation of the FR properties proportional to the quantity of ZB. On the contrary, the influence of ZB in the mixtures containing 20% of additives is minor: slight increase in the pHRR value with 1%ZB and similar values for the 20%APP and 18%APP/2%ZB samples.

Thus the comparison between all the intumescent reprocessed PP/EPR/EO formulations shows that the best results are also obtained with 20% of APP. Here, the presence of ZB has no influence on the FR properties. The presence of mineral additives in the EO could explain these results because the reduction of the pHRR value is much more pronounced for the reprocessed 20%APP/PP/EPR/EO than for the 20%APP/PP/EPR (77% decrease against 61%), compared to their respective reference material. It may be explained by considering that the degradation products of the EO react with those of APP, improving the efficiency of the char structure. The quantity of mineral additives inside the EO is sufficient to achieve the same fire performance as with 1%ZB because similar pHRR values are obtained for the reprocessed 20%APP/PP/EPR/EO and the non-reprocessed 19%APP/1%ZB/PP/EPR, respectively 64 kW/m^2 and 56 kW/m^2. Then, the incorporation of an additional quantity of ZB (1 or 2%) in the reprocessed materials does not permit to improve the FR properties. This phenomenon has been previously observed for the non-reprocessed material where the 18%APP/2%ZB/PP/EPR sample gave a slightly higher pHRR value than the 19%APP/1%ZB/PP/EPR one.

Evaluation of Swelling

The formation of a carbonaceous layer at the surface of the material has been observed for all the intumescent formulations. Nevertheless, the presence of this char is not sufficient to bring good FR properties. The efficiency of an intumescent system is also driven by the physical properties during the intumescent process, particularly to its ability to expand and form a multicellular structure.[18] Therefore, some investigations on protective layer thickness and expansion rate were carried out to find a correlation with fire performance.

Non Reprocessed and Non Polluted Materials

Thanks to the protocol described in the experimental section, the expansion of intumescent PP/EPR materials as a function of time can be obtained by image analysis (Figure 4). The expansion is very fast for all the samples because they begin to swell immediately after the beginning of the experiment. Within one minute, the samples thickness is at least twofold.

To compare easily the behaviour of the different formulations, the average expansion rates within the first 50 seconds have been determined from Figure 4 (Table 2). The final char height deduced from Figure 4 and the pHRR values obtained by mass loss calorimetry are also mentioned in Table 2.

The average expansion rates obtained within the first 10 seconds are of the same order for all the samples with values slightly superior for the 19%APP/1%ZB and 18%APP/2%ZB materials. For longer times of experiment (between 10 and 50 seconds), this tendency becomes more marked because the expansion rate is much higher for the two afore-mentioned formulations. These results are consistent with the values obtained by mass loss calorimetry and give evidence that the higher the expansion rate, the better the FR properties. In fact, the char acts as a thermal insulative barrier between the flame and the virgin material. This enables the combustion cycle to be stopped as early as possible.[19] Here, the expansion occurs very rapidly and the APP/ZB mixture can consequently suffocate the flame, which can explain the FR performance of these materials. Now, considering the final thickness of the carbonaceous layer, the same value (18mm) is obtained for the 19%APP/1%ZB, the 20%APP and the 9%APP/1%ZB samples namely respectively the

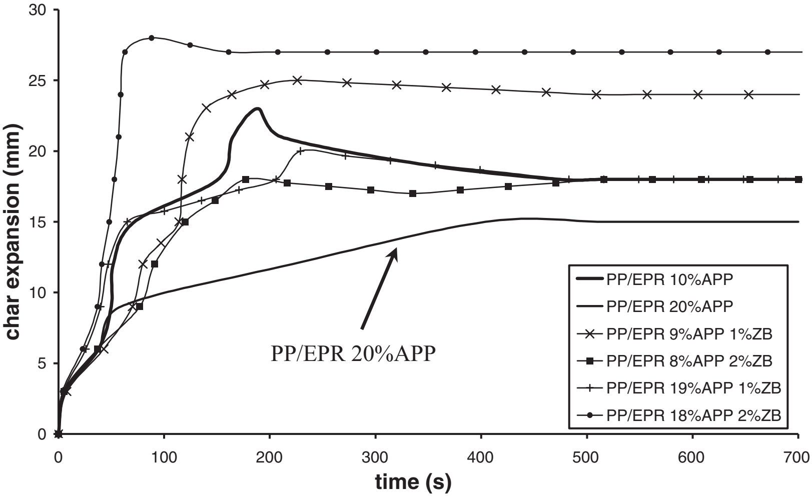

Figure 4.
Evolution of the char expansion as a function of time for the non-reprocessed PP/EPR blends.

lowest and the two worst pHRR values. Therefore, the char thickness and the fire performance of a material are not correlated.

Reprocessed PP/EPR/EO Materials

Figure 5 describes the evolution of char expansion as a function of time for all the samples based on reprocessed PP/EPR/EO. Deduced from these curves, the different expansion rates along with the final thickness of the carbonaceous layers are given in Table 3.

By comparing the materials containing 10% of additives, the highest swelling rate is obtained for the 10%APP sample, whatever the time considered. And once again, the expansion rate seems to be correlated to the FR properties because the pHRR value of the 10%APP is inferior to the 9%APP/1%ZB and 8%APP/2%ZB formulations. In the case of the materials containing 20% of intumescent additives, the expansion rate is the highest for the 20%APP formulation within the first 10 seconds. On the contrary, for longer times (10s < t < 50s), this rate is superior for the 18%APP/2%ZB formulation. But it is noticeable from Figure 5 that until 45 seconds of experiment, the average expansion rate is similar for the 20%APP and the 18%APP/2%ZB formulations. Thus, it can explain why the pHRR values are of the same order for these two samples, confirming the relationship between the expansion rate of the char and the fire performance.

Once again it can be seen that there is no correlation between the final char thickness and the FR properties because the lowest swelling (21mm) is obtained for a sample having relatively good fire properties. In fact, previous studies[17,19] have pointed out

Table 2.
Physical parameters relative to char expansion for the non-reprocessed PP/EPR blends.

	10%APP	9%APP 1%ZB	8%APP 2%ZB	20%APP	19%APP 1%ZB	18%APP 2%ZB
Average expansion rate (mm/s) for $t < 10s$	0.338	0.317	0.347	0.345	0.371	0.395
Average expansion rate (mm/s) for $10s < t < 50s$	0.141	0.090	0.088	0.106	0.220	0.306
Final thickness (mm)	18	24	18	15	18	27
pHRR (kW/m^2)	220	145	191	174	56	86

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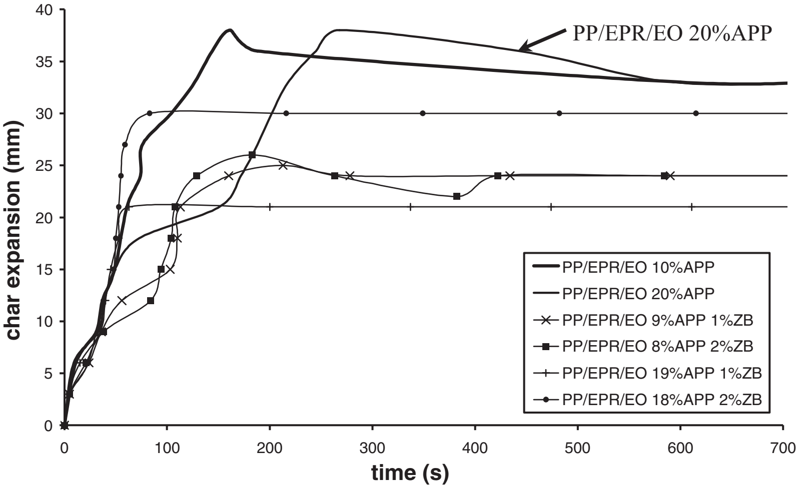

Figure 5.
Evolution of the char expansion as a function of time for the reprocessed PP/EPR/EO blends.

that there must be a correlation between expansion and rigidity of the protective layer i.e. the right structural organization of the char (e.g. cell structure, cell distribution, size of the cells…) to obtain efficiency in the FR properties.

Conclusion

In this work, the influence of pollution and reprocessing on the reaction to fire of high impact PP intumescent formulations has been investigated. It has been demonstrated that for the two types of mixtures, the best results were obtained with 20% of additives. Nevertheless, ZB acts as a synergistic agent in the case of the original PP/EPR blends because reaction between the degradation products of APP and ZB leads to the formation of borophosphates which are more resistant to high temperatures. Considering the reprocessed PP/EPR/EO blends, ZB has no influence because of the presence of minerals inside the engine oil that act as a flame retardant. The importance of the swelling rate at the beginning of the intumescent process has been highlighted thanks to the use of an innovative device which demonstrated that the fire performance of a material was correlated to the fastness of char formation.

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Table 3.
Physical parameters relative to char expansion for the reprocessed PP/EPR/EO blends.

	10%APP	9%APP 1%ZB	8%APP 2%ZB	20%APP	19%APP 1%ZB	18%APP 2%ZB
Average expansion rate (mm/s) for $t < 10s$	0.545	0.379	0.394	0.613	0.464	0.383
Average expansion rate (mm/s) for $10s < t < 50s$	0.251	0.183	0.146	0.225	0.306	0.354
Final thickness (mm)	33	24	24	33	21	30
pHRR (kW/m^2)	144	171	208	64	93	53

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