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PREPARATION AND CHARACTERIZATION OF POLYPROPYLENE/RUBBER POWDER BLENDS CONTAINING TWO FLAME RETARDANT SYSTEMS INTENDED FOR THE AUTOMOTIVE INDUSTRY

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Keywords: post-consumer materials, flame retardancy, recycling, sustainability, automotive industry

Abstract
Two series of polymer blends based on post-consumer materials, i.e. postconsumer polypropylene (rPP) and rubber dust (Rd) under the trademark ECOPLASTOMER® PP70 with a mutual ratio of components 70/30 wt.% containing 10, 20, and 30 wt.% of flame retardants, have been prepared using a twin-screw extruder. The influence of commercially available silane-treated alumina trihydrate (ATH-sil) with the eco-friendly system based on melamine phosphate (MP), aluminum hydroxide oxide (AC), and peanut shells (PS), used as flame retardant agents on the mechanical, thermal, and flammability properties of polymer blends was assessed. The incorporation of ATH-sil results in the appearance of peaks related to OH groups, with higher intensity for increased ratio of filler; similar observations are made for the MP-AC-PS system, although mainly finding the P-OH from MP, Al-O from AC. DSC analysis revealed that the inclusion of the selected flame retardants did not impact the melting and crystallization temperatures of the polymer matrix. Conversely, an attenuation in the melt flow rate of the composites was observed with increasing proportions of both additives, leading to enhanced rigidity, elevated elastic modulus, and diminished elongation at break following a similar pattern. Tensile strength experienced a minor decrease, particularly in composites containing more than 20% of the flame retardants, while hardness remained unaffected by their integration. Both flame retardants diminished the combustibility of the modified polypropylene/rubber powder blends; nevertheless, the most favorable outcomes were achieved with ATH-sil, especially when employed at a minimum of 30wt%. The formulated MP/AC/PS

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system proved more adept at diminishing combustibility and smoke emissions at lower levels of flame retardants.

1. Introduction

Currently, heightened awareness of environmental issues and regulatory measures has compelled producers to assume responsibility for plastic recycling in their efforts to fulfill global demand [1]. The global production of polyolefins has increased by over 1000% since the 1950s. The amount of municipal waste based on these polymers each year is 2.1 Bt. Environmental regulations have increased consumer awareness and producers' responsibility for plastic recycling. Plastic recycling, especially polyolefins, is important in its potential to conserve resources, reduce waste, and contribute to a circular economy [2].

On the other hand, the flammability of polymers has been recognized as a social and scientific problem in many industries, including the automotive industry [3]. Improving flammability resistance in the automotive industry is rooted in safeguarding lives, meeting safety standards, enhancing public trust, and minimizing the impact of accidents on individuals and the environment. It is a critical aspect of overall vehicle safety and contributes to the ongoing evolution of automotive technology.

Efficient technology and applications for recycled polymer waste have become increasingly important to decrease environmental contamination and conserve nonrenewable fossil fuels. Therefore, in the present work, one has compared the effect of commercially available silane-treated alumina trihydrate (ATH-sil) with the eco-friendly system based on peanut shells, melamine phosphate, and aluminum hydroxide oxide, used as flame retardant agents on the mechanical, thermal, and flammability properties of polymer blends consisted of postconsumer polypropylene (rPP) and rubber dust (Rd) under the trademark ECOPLASTOMER® PP70. Two series of composites based on rPP/Rd with a mutual ratio of components 70/30 wt.% containing 10, 20, and 30 wt.% of flame retardants, have been prepared using a twin-screw extruder. The chemical characterization of the compositions was analyzed using FTIR spectroscopy. The mechanical properties, hardness, and melt flow index (MFI) of the compositions have been assessed. The thermal properties have been studied using differential scanning calorimetry (DSC). Finally, the flammability of the compositions has been analyzed using cone calorimetry measurements to select the most efficient flame retardant system (CC).

2. Materials and methods of characterization

2.1. Materials

The polymer matrix used in this study was the blend of post-consumer polypropylene with rubber dust in the combination of 70/30 under the trademark ECOPLASTOMER® PP70 provided by Ecopolplast sp. z o.o. As the flame retardants one used the following materials presented in Table 1:

Table 1. Characterization of the used flame raterdants

Flame retardant	ATH-sil	MP	AC	PS
Characterisation	surface modified alumina trihydrate Apyral 40 VS1 (Nabaltec, Schandorf, Germany), vinyl silane treated mineral flame retardants with 98.5% content of $Al(OH)_3$, the specific surface area of 3.5 m^2/g, bulk density of 350	Melamine Phosphate, Exflam MP (Wellchem Chemicals, Zhejiang, China), with phosphorus wt % of min. 12%, nitrogen wt % of 36-38%, density 1.74g/cm^3, Particle size D50 of 10μm	ACTILOX® B60 (Nabaltec, Schandorf, Germany) is boehmite mineral-based flame retardant, with 99% content of AlOOH, the specific surface area of 5.0 m^2/g, bulk density of 400 kg/m^3, whiteness of 98%	peanut shells (*Arachis hypogaea L. species*) were provided by local suppliers (Poland, Central Europe), and drying process was conducten for 7 days at 65 ± 5 °C, while grinding on a laboratory sieve mill L-0210 from Cloer

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kg/m³, density of
2.4 g/cm³

2.2. Preparation of the samples

Two series of PP70-based compositions containing ATH-sil (series I) and the system of MP/AC/PS (series II) were prepared on a counter-rotating twin-screw extruder (LSM30, Leistritz Laborextruder) with closely overlapping coils and interchangeable mixing sections (diameter D = 34 mm, L/D ratio = 23) equipped with a set of gravimetric feeders, which dosed the set proportion of the components. Materials were dried in a dryer under a dynamic vacuum before extrusion. The temperature of the extrusion process was selected based on the DSC analysis for PP70 and the thermal degradation temperatures of the system containing among others peanut shells. The rotational speed of the screws of 40 rpm. Yield: 2.0 kg/h. The obtained materials were pelletized and injection molded using Boy 35 (Dr BOY GmbH&Co., Neustadt, Germany) to obtain dumbbell shape samples, type ISO 37 type A3, for tensile measurements.

2.3. Characterisation methods

Attenuated total reflectance – Fourier Transform Infrared (ATR-FTIR) spectra of the analyzed materials were recorded using FTIR spectrophotometer Perkin Elmer Two (Perkin Elmer) with 64 scans and a resolution of 4 cm-1 over the frequency range of 4000-400 cm^{-1}.
The differential scanning calorimetry (DSC) was performed using a DSC 204 F1 Phoenix (Netzsch, Selb, Germany) thermal calorimeter under a nitrogen atmosphere in the heating-cooling-heating cycle, with the heating/cooling rate of 10 °C/min, from -85 to 250 °C and sample weight 10±0.2 mg. The crystallization temperature (T_c) and melting temperature (T_m) were determined from the maximum of the exothermic and endothermic peaks, respectively. The heat of fusion (ΔH_m) and crystallization (ΔH_c) were calculated from the total areas under melting and crystallization peaks on the DSC curve.
Using cone calorimeter measurements performed on the Fire Testing Technology apparatus, following the ISO 5660-1 and ISO 5660-2 procedures, the burning behavior of investigated materials was assessed. The horizontally oriented samples were irradiated at a heat flux of 35 kW/m², and spark ignition was employed to ignite the pyrolysis products. An optical system with a silicon photodiode and a helium-neon laser provided a continuous survey of smoke. Three tests were made for each series, and the residues were photographed using a digital camera.
Melt flow rate (MFR) measurement has been performed using A-MeP EXTRUSION PLASTOMETER, Noselab ATS (Italy). Tests were carried out according to ISO 1133 standard at 230°C and under a load of 2.16 kg.
The static mechanical properties were carried out using EZ-TEST-LX universal testing machine (Shimadzu, Kyoto, Japan) equipped with a 1 kN Shimadzu load cell, digital extensometer TRViewX-500D, and TRAPEZIUM X software. Stress-strain tests were performed at room temperature, with a crosshead speed of 25 mm/min to break at room temperature. The reported values are the mean values of five measurements. The measurements were performed according to PN-EN ISO 527.
The Shore D hardness was measured using a manual shore test stand SAUTER TI, (Germany). The reported values are the mean of 10 independent measurements.

3. Results and discussion

The structure of PP70-based compositions containing two systems of flame retardants was investigated using FTIR spectroscopy (Figure 1). For the reference material (PP70) one could have observed the

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absorption peak located at 840 cm^{-1} assigned to C–CH$_3$ stretching vibration, and absorption peaks displayed at 972, 997, and 1165 cm^{-1} assigned to –CH$_3$ rocking vibration. In turn for all samples, both with the addition of ATH-sil and the MP/AC/PS system, the symmetric bending vibration mode of –CH$_3$ group at 1375 cm^{-1}, absorption peak at 2952 cm^{-1} related to –CH$_3$ asymmetric stretching vibration, as well as absorption peaks at 1455, 2838, and 2917 cm^{-1} attributed to –CH$_2$– symmetric bending, –CH$_2$– symmetric stretching and –CH$_2$– asymmetric stretching, respectively, were detected [4]. this band overlaps the OH vibration in Al(OH)$_3$ (3621-3281 cm^{-1}), which is more significant for the higher content in ATH in the final composite. For the green IR system proposed, the most significant differences with the spectrum for the PP70 are in the appearance of a sharp peak at 1665 cm^{-1} (P-O-H in melamine phosphate), 1077 cm^{-1} (Al-O bonds in AC), and a wide band from 700-500 cm^{-1} (P-O in MP and Al-O in AC) [5-7].
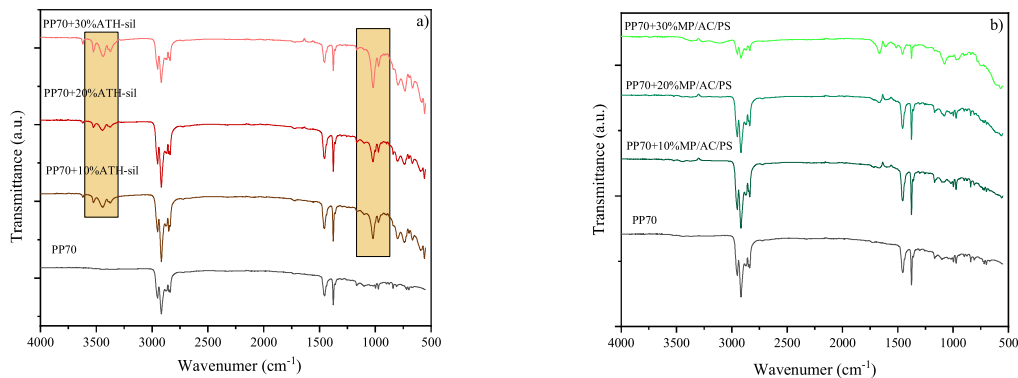

Figure 1. FTIR spectra of PP70-based compositions containing two systems of flame retardants.

Phase transition temperatures were investigated with the use of DSC analysis. The DSC thermograms are presented in Figure 2. Due to the fact that post-consumer PP, which was the basis for PP70, contained a small amount of polyethylene (PE), melting and crystallization peaks were expected in the thermograms for both PP and PE. In fact, the phase transitions related to the melting and crystallization of both of these pololefins were detected in the thermograms recorded during heating and cooling. The melting temperature that comes from PP in PP70 was found to be Tm = 163.2 °C. Moreover, PP70 crystallized during cooling with a crystallization temperature of 120.7 °C. However, observing the phase transition temperatures for both series of compositions with the addition of flame retardants, no significant changes in the melting and crystallization temperatures were observed. They were also at a level of about 1-2°C. Similarly, no differences were observed in the melting and crystallization enthalpy values corresponding to the analyzed phase transformations.
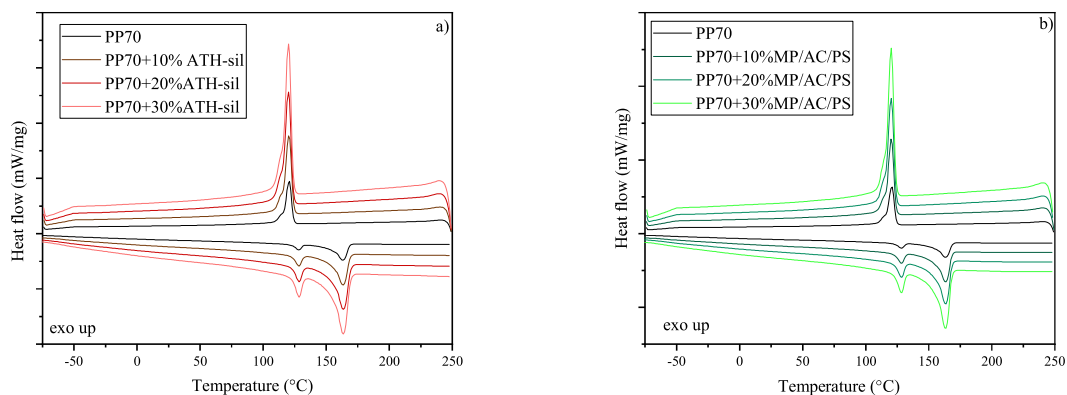

Figure 2. DSC thermograms recorded during 2nd heating and cooling of PP70-based compositions containing two systems of flame retardants.

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The impact of developed flame retardant systems on the polymers' burning behavior was assessed via cone calorimetry tests. The heat release curves (HRR), photographs of residue, and data obtained from measurements are presented in Figures 3-4 and Table 2, respectively.
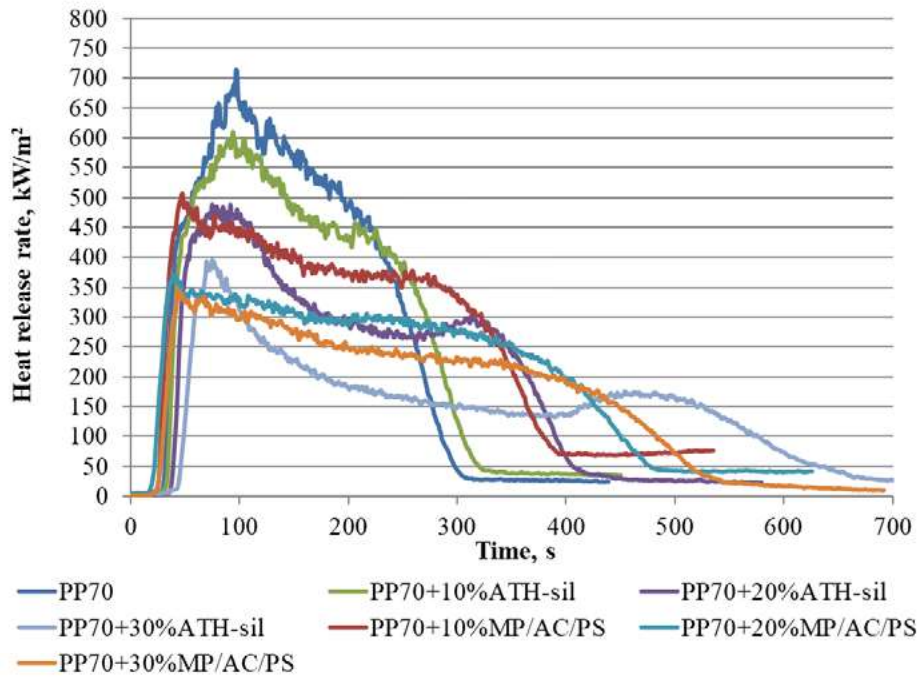

Figure 3. Representative heat release rate curves of investigated materials

As shown in Figure 3, PP70 exhibited one broad peak with the maximum heat release rate (pHRR) equal to approx. 760 kW/m2. Employing ATH-sil resulted in a gradual decrease in the HRR, and the lowest values were achieved for the material with the highest flame retardant content. ATH extended the time needed for the material to heat up to the ignition temperature (Fig. 3), and the release of water vapor reduced the concentration of free radicals and oxygen. Moreover, a layer of Al_2O_3 is formed on the surface of the polymer, which prevents the heat and oxidant from propagating to deeper layers of the material (Fig. 4). MP worked mainly in the condensed phase, while AC increased the ability to form a char and replaced the polymer with a less flammable component. In turn, the structure of PS, rich in polar groups, enhanced the effectiveness of phosphorus flame retardant in char formation (Fig. 4). The combination of MP, AC, and PS flattened the curves, characteristic of materials able to form a char.

Figure 4. Photographs of the samples after cone calorimetry tests

The highest values of time to ignition (TTI) were recorded for a series of materials with ATH, which is connected with the flame retardant's mechanism of action described above. In turn, the developed system

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led to a decrease in TTI due to the earlier decomposition of phosphorus flame retardant. The lowest pHRR, two times lower than the unmodified polymer, was obtained for PP70+30%MP/AC/PS. Hovewer, the highest reduction in the maximum average rate of heat emission (MARHE), as one of the essential indicators enabling flame spread evaluation, was noted for PP70+30%ATH-sil. The reduction of total heat release (THR) results from incomplete combustion caused by char formation and reduced combustion efficiency, confirmed by lower effective heat of combustion (EHC). Similarly, the lowest values for both THR and EHC were observed for PP with 30% of ATH-sil. The use of large amounts of this flame retardant also resulted in the most significant reduction in smoke emissions, assessed based on total smoke release (TSR), which results from the dilution of the gas phase. It should be noted that although ATH showed the best effectiveness in reducing burning and smoke emissions, this effect was achieved only when its share was 30% by mass. For the remaining shares (10 and 20%), lower parameter values were repeatedly recorded for the MP system /AC/PS.

Table 2. Cone calorimeter results for polymers with fire retardant systems

Materials	TTI (s)	pHRR (kW/m^2)	MARHE (kW/m^2)	THR (MJ/m^2)	EHC (MJ/kg)	TSR (m^2/m^2)
PP70	37±2	756±87	472±12	124±1	39±0	2218±115
PP70+10%ATH-sil	39±2	602±29	409±20	122±1	38±0	2148±46
PP70+20%ATH-sil	42±1	493±22	311±10	116±2	36±1	1979±98
PP70+30%ATH-sil	45±2	398±12	209±6	106±2	34±1	1535±52
PP70+10%MP/AC/PS	30±3	502±27	359±26	126±10	39±3	2168±154
PP70+20%MP/AC/PS	27±2	371±4	269±12	120±5	37±2	1801±120
PP70+30%MP/AC/PS	31±1	344±12	249±14	120±20	37±4	1841±108

Table 3 summarizes the data obtained from melt flow measurement, hardness and tensile tests. It was found that along with the incorporation of flame retardants, a decrease in the MFR was observed. A much more intense impact on the MFR value was observed for the MP/AC/PS system. This might result from the interfacial interactions between the additive and the polymer matrix, which can hinder the mobility of polymer chains, making it more difficult for the polymer to flow and reducing the melt flow rate. Moreover, a stiffening nature of the addition of modifiers was observed, which is reflected in the increase in the value of Young's modulus and decrease in elongation at break. The most intense increase in E was observed for the system containing 30% ATH-sil and it was an almost two-fold increase. The elongation at break values were also significantly reduced for the composition containing the highest amount of flame retardants (30%). In turn, there were practically no changes in the hardness of the materials, and the TS value decreased slightly with the increase in the amount of flame retardants in the system.

Table 3. Melt flow rate and mechanical properties of the series of PP70-based compositions containing flame retardants

Material	MFR (g/10min)	H (°ShD)	E (MPa)	TS (MPa)	ε_b (MPa)
PP70	6.72±0.3	67.8±0.9	615±98	21.4±0.4	35.7±3.3
PP70+10%ATH-sil	5.26±0.2	67.0±0.5	825±128	20.7±0.3	31.6±5.6
PP70+20%ATH-sil	5.13±0.2	67.9±0.6	1031±141	17.6±0.7	21.2±3.7
PP70+30%ATH-sil	4.15±0.1	67.9±0.7	1290±198	17.4±0.2	18.4±1.3
PP70+10%MP/AC/PS	4.77±0.1	67.1±1.0	649±178	20.7±0.4	31.8±0.9
PP70+20%MP/AC/PS	4.32±0.6	67.0±0.8	931±112	18.7±0.8	31.1±1.1
PP70+30%MP/AC/PS	3.37±0.3	69.0±0.9	950±147	17.9±1.3	21.5±2.7

MFR – melt flow rate; H- hardness; E- Young's modulus; TS – tensile strength; ε_b – elongation at break

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3. Conclusions

Two series of composites based on post-consumer PP with 30wt.% of rubber dust containing 10, 20, and 30 wt.% of two systems of flame retardants, have been prepared using a twin-screw extruder. The structure and composition of the analysed systems were investigated utilizing FTIR spectroscopy. In the case of ATH-sil containing compositions, one observed characteristic absorption bands at 661 cm^{-1} and 963 cm^{-1} related to the Al–O stretching vibrations, as well as the stretching NH$_2$ vibration at 3452 cm^{-1}, which were due to surface modification by the silane coupling agent. For MC/AC/PS composites, the main changes are due to the vibration of P-OH in MC and Al-O in AC. In addition, the mechanical properties, hardness, and melt flow rate (MFR) of the compositions have been assessed. The thermal properties have been studied using differential scanning calorimetry (DSC). DSC studies showed that the addition these selected systems of flame retardants caused no effect on the melting and crystallization temperatures of PP70. On the other hand, a reduction of melt flow rate of the composites is obtained with the increased ratios of both fillers, which also provide a stiffening effect, increasing the elastic modulus and reducing the elongation at break with the same trend. Tensile strength was slightly reduced, particularly for composites with over 20 % of the flame retardants, while hardness was not affected by the incorporation of any of them. Both flame retardants reduced the flammability of modified polypropylene/rubber powder blends; however, the most beneficial effects were obtained for ATH-sil, employing at least 30wt%. The developed MP/AC/PS system was more effective in reducing flammability and smoke emissions for the lower share of flame retardants.

Acknowledgments

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