proceedings

Original research

The studies on the production of polyethylene film with reduced flammability

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Received: 22/10/2017

Abstract: A Natural and synthetic polymers and plastics made of them, are an integral part of the urban environment in many different areas. Polyethylene is one of the most widely used polymers. Production of films of different kinds and purposes is determined by the specific properties of polyethylene. Among the polymers and polymeric materials only a small portion can be considered non-flammable. The vast majority (including the above-mentioned polyethylene) undergoes a process of thermal destruction under the influence of a sufficient amount of energy, emitting a considerable amount of heat and smoke. Studies on the flammability of polymers and methods of its reduction are driven by factors of ecological, economic and safety aspects. The experimental section describes a procedure for preparing a film material and a comparison of properties, with respect to the used filler: colloidal silica, calcium phosphate or hydroxyapatite. With Differential Scanning Calorimetry (DSC) we tested properties such as melting and crystallisation temperature, heat of fusion and the content of crystalline phase. Studies were carried out using the flammability test LOI UL-94 and microcalorimetry of pyrolysis-combustion to determine the burning rate, the limiting oxygen index as well as the rate and the amount of released heat. Optical microscopy was also used to examine the morphology of the polymer matrix. On the basis of the results, the modification of polyethylene matrix was found effective. The addition of fillers had a significant impact on the mechanism of combustion of the investigated films. It revealed a reduction in burn rate, a reduction in rate and amount of released heat and an increase of the value of LOI. At the same time, there were no significant effects on the other properties of the composites. The most prominent flame retardant effect as compared to a pure polyethylene film was provided by hydroxyapatite. There was no occurrence of synergistic effect between the phosphorus compounds and the silica, so there is no reason to apply them in such combination as a mixture of fillers, giving the effect of fire retardant in the composite material.

Keywords: polyethylene films, flammability, flame retardants.

1. Introduction

Natural and synthetic polymers and plastic based materials are an inherent part of the urbanized environment of modern man in the fields of life such as transport, 1]. Production of plastics in Poland In 2014 it amounted to over 3 million tones, and in 2015 over 3.3 million tones, which is the result about 9% higher than in the previous year [2]. Only a small proportion of polymers and polymers can be considered non-flammable. The remaining majority is thermodestructured under the action of sufficient energy, leaving a significant amount of heat and smoke. In the event of fire, approximately 4,000 people die in the United States and about 5,000 in Europe each year. Losses from fire accidents are about 0.3% of GDP. According to the Geneva-based Aircraft Crashes Record Office (ACRO) in the years 2001-2010, 1662 official catastrophes have been reported with nearly 16,000 fatalities. After analyzing the causes of various air events, it was found that by reducing the flammability of composite polymeric materials, the drastic nature of these accidents could be reduced [1]. These data show that environmental and economic factors and, most importantly, the need to protect health and life are the driving force for polymer flammability studies and at the same time on ways to lower it.

Polyethylene is one of the most widely used polymers in the aforementioned fields of life. It represents approximately 12% of total plastics production in Poland, and the increase in polyethylene production from 2014 to 2015 was about 15% [2]. High-density polyethylene (HDPE), medium (MDPE) and low (LDPE) density can be distinguished. Another criterion for the distribution of polyethylene is its molecular weight. For example, polyethylene with ultra high molecular weight Mw> 3000000 can be distinguished, whereas high molecular weight polyethylene is usually within the limits of 130000> Mw> 1000000 [3]. Such properties of products. Polyethylene such as tear strength, tensile strength, impact strength, rigidity and transparency determine its use for the production of films of various types and destinations. These include, but are not limited to: sacks and food foils, sacks intended for shipment of goods, stretch lining and shrink films [3].

Taking into account the above-mentioned applications, and hence the need to preserve the proper properties of polyethylene films (including reduced flammability), there is a need for continuous improvement of production at every possible stage. There are also many new patents and publications on innovative solutions in the field of polyethylene film production. The most commonly used are multilayer composite films in which individual layers. The specific chemical compositions are responsible for the specific property.

2. Materials and Methods

3.1. Materials used

3.1.1. Polymer matrix

The polymer matrix was polyethylene (PE) produced by Basell Sales & Marketing Company B.V. in Rotterdam named PUREL ACP 6541A, characterized by a melt index (190°C / 2.16 kg): 1.45g / 10 min.

3.1.2. Nanofiller

The main filler was hydrophobic colloidal silica (ASI), purchased at Evonik Corporation USA in Parsippany under the trade name AEROSIL R974. Hydrophobic colloidal silica modified with dimethyldichlorosilane (as provided by the manufacturer) was obtained on the basis of hydrophilic colloidal silica with a specific surface area of 200 m^2/g.

3.1.3. Other additives that act as flame retardants

In the experimental work, calcium phosphate (FOS) and hydroxyapatite (HAP) were used as potential flame retardants for polyethylene film. Both FOS and HAP were received at the Department of Inorganic Technology and Environmental Biotechnology of Cracow University of Technology.

3.2. Film production

Composite films were obtained by homogenization in the molten state of the polymer. Premixing of the polymer matrix and filler was carried out in a mixer. The total weight of each mixture was 1 kg. The composition and designations of the individual compositions are shown in Table 1.

Table 1. Made compositions with markings

Sample designation	**Content of additive [% mass]**		
	Calcium phosphate	**Hydroxyapatite**	**Aerosil R974**
PE	-	-	-
PE/FOS	3	-	-
PE/HAP	-	3	-
PE/ASI	-	-	3
PE/ASI/FOS	1.5	-	1.5
PE/ASI/HAP	-	1.5	1.5

The twin screw extruder had a cylinder divided into nine heating zones. The screw diameter was 24 mm, having a standard profile for extrusion of polyolefins. A special angular head for extrusion of the film is attached to the cylinder module, divided into two heating zones. The film receiving unit was equipped with a film feeder in the form of cooled, rotating gallons and a rotary spindle receiver.

The first experimental work related to the production of polyethylene film was based on the final conditions of extrusion of polyethylene film, ie the temperature of the individual cylinder heating zones and the angular head, the speed of the screws, the speed of the spindle and the gallon, as well as the gallon temperature. Tables 2 and 3 show the final conditions for obtaining and receiving polyethylene composite film. The films obtained had a thickness in the range of 0.30 to 0.72 mm.

Table 2. Film extrusion conditions

Extrusion												
Temperature of heating zones [°C]	**Screw**									**Connector**	**Head**	
	I	II	III	IV	V	VI	VII	VII	IX		I	II
	160	200	200	200	200	200	200	200	200	200	250	250
Rotational speed of screws [rpm]	50											

Table 3. Conditions for receiving film

Receiving		
Receiving speed [m/min]	**Spindle**	**Gallons**
	5.2	3.8
Temperature [°C]	-	26

3.3. Flammability testing methods and apparatus

Flammability testing methods included: UL-94 flammability measurements in a vertical system in accordance with standard [4], determination of the LOI with standard [5]. Microcorrimetric studies were also carried out using pyrolysis pyrolysis and PCFC Fire Testing Technology Ltd. according to standard [6].

The UL-94 flame retardant test specimens were 125 mm ± 5 mm in length, 13.0 mm ± 0.3 mm in width, and the thickness was not greater than the width. The mean thickness of the samples tested is set forth in Table 4. Temperature in the laboratory measured at 23°C. Each of the samples, when attached to the handle, was exposed to a gas burner flame for not more than 10 seconds. For accurate analysis of the combustion process, the determination of the burning times and the number of detachable droplets of the burning material, video recording was performed using a digital camera. Five replicates were made for each composition, and the results were averaged.

The limiting oxygen concentration (LOI) is the minimum oxygen concentration (expressed in % vol.) in a mixture with nitrogen, which, under the conditions prevailing during the test, allows the combustion of the test sample to continue with the flame [5]. Samples for the LOI limit gauge were matched to the standard handle. The temperature in the laboratory during the measurement was 23°C. Each of the samples was flamed with a gas burner for no longer than 10 seconds. The gas flow in the camera was set to 10 l/min. Two series of measurements were made: a test in the direction perpendicular to the film extrusion axis and a test in the direction parallel to the film extrusion axis. For each composition, 7 to 13 samples were used in one measurement series. The results are summarized in Table 5.

Microcalorimetry measurements were made on samples of approximately 5.5 g weight in corundum (α-Al_2O_3) crucibles. The temperature was set at 900°C. The heating rate was 1°C/s. An atmosphere of 80% vol. with nitrogen and 20% vol. with oxygen. Total gas flow was set to 100 cm^2/min. The results are shown in Figures 1 and 2.

3. Results and Discussion

3.1. Measurement by UL-94 method

When analyzing the results of the UL-94 flammability test, all samples were completely burned. The general mechanism of combustion of individual samples was similar. Initiation of the ignition of the samples posed some difficulties due to the small thickness and flexibility of the tested strips. Under the influence of the applied burner flame, the test profiles were bent and curled up. In spite of this, arson of the test specimen was fast, most often at the first contact of the burner flame with the test sample. At the beginning of the burning of the material, the appearance of the yellow flame from the combustion of the sample material was considered. During the test, it could be concluded that the incineration was rapid in each of the samples tested. After initiating the fire, the flame moved up the sample to increase its size. It was evident that the stripes were melting, Immediately after, the beginning of the droplets of burning material was observed. The phenomenon occurred quickly, the drops were tearing apart at short intervals. In any case the drops were small in size. No large pieces of burning material were peeling away. For each test composition, the burning material was lit by a cotton fabric placed underneath the sample. The smoke that was emitting was black, but it did not whirl, but it was a thin flame over the flame. Accompanying the burning smell was similar to the smell of a burning paraffin candle. All samples were completely burned. The length of the individual samples (according to the standard) was about 125 mm, they were fixed in the holder at a distance of 5 mm from the edge, resulting from the provisions in Table 4.

Table 4. UL-94 flammability test in vertical system

Sample	**Length of the burned sample [mm]**	**Thickness of the sample [mm]**	**Czas spalania [s]**	**Burning time [mm/s]**	**Number of drops**	**UL-94 V**
PE	120	0.30	17	440	47	-
PE/FOS	120	0.52	25	280	77	-
PE/HAP	120	0.30	21	340	63	-
PE/ASI	120	0.72	44	160	66	-
PE/ASI/FOS	120	0.46	29	250	69	-
PE/ASI/HAP	120	0.35	19	400	49	-

The analysis of video recordings of individual samples allowed for detailed observation of differences in the course of burning the films obtained according to subsequent recipes. The reference sample, containing only PE, contained the shortest average burning time. At the same time the process proceeded in the most violent way. For this composition, the average burning speed was

440 mm/s. The short burn time and high speed had an effect on the amount of detachable droplets of burning material, which averaged 47 and was the lowest result among the films tested. PE/HAP and PE/ASI/HAP were characterized by similar parameters during combustion. It should also be noted that the average thickness of the samples from these test compositions was similar and was 0.30 mm for PE/HAP and 0.35 mm for PE/ASI/HAP respectively. The PE/HAP composition compared to PE/ASI/HAP burned on average for a long time, thus reducing the speed of combustion. This allowed us to detach more droplets of burning material. In the case of PE/FOS and PE/ASI/FOS composition, the differences were not so significant. Despite the fact that the average thickness of PE/FOS samples (0.52 mm) was higher than the PE/ASI/FOS samples (0.46 mm), the PE/ASI/FOS samples burned longer and slower. In addition, when dripping PE/FOS samples dripping was more violent, so that the average number of detached droplets was the highest among all tested compositions. The PE/ASI composite had the longest average burning time and the lowest combustion speed. However, the average thickness of the samples to be tested should be taken into account. The PE/ASI composition was 0.72 mm.

3.2. Determination of limit oxygen indicator (LOI)

Determination of the oxygen indicator was started on samples for which the orientation during combustion in the measuring device was perpendicular to the extrusion axis. The study started with a reference sample containing only PE. The estimated LOI value for this sample was 17.7% [5], so it was chosen as the start value of the oxygen content (in % vol.) In the mixture with nitrogen. The final measurement results are summarized in Table 5. The PE reference samples behaved in two ways during the study. In the course of the measurement, when the percentage of oxygen in the gas mixture flowing through the device to a value lower than the final LOI value was set, the samples after contact with the flame of the gas burner lit for a period of about 1-2 seconds and then extinguished. There was also a complete lack of fire handling of the samples tested. The samples were over-melted under the influence of short-time exposure to the burner flame, but no effects were observed such as dripping or charring of samples. After removing the burner flame, the molten sample material immediately froze. On the other hand, when the percentage of oxygen in the gas mixture flowing through the instrument was higher than the limit value needed to sustain the combustion, the samples were burned almost completely. After a brief contact with the flame of the gas burner, the material dealt with fire and burned with a yellow flame. However, no significant smoke evolution has been observed. Accompanying the burning smell was similar to the smell of a burning paraffin candle. Burning proceeded the fastest in the vertical axis of the sample, where the flame was facing. The rapidly moving front of the flame reached the specified distance on the handle within a few seconds, which allowed for unambiguous determination that the sample was to be declared flammable at the given oxygen content of the gas mixture.

Table 5. UL-94 flammability test in vertical system

Sample	**LOI [%]**	
	A sample attached perpendicular to the direction of extrusion	**A sample attached parallel to the direction of extrusion**
PE	19.3	19.6
PE/FOS	30.2	19.9
PE/HAP	33.0	20.1
PE/ASI	24.5	17.1
PE/ASI/FOS	25.0	20.1
PE/ASI/HAP	27.4	19.1

The nature of combustion of the remaining compositions containing the additives used and their combinations was different from the reference sample containing pure PE. However, a great similarity was observed in the combustion of all remaining compositions. As the starting point, the LOI value for the PE composition was 19.3%. The incineration of any composite film was not supported at this oxygen content in the gas mixture flowing through the apparatus. At relatively low concentrations of oxygen, close to the reference sample, the tested samples of all compositions did not deal with fire when exposed to the burner flame. As in the case of PE samples, they slightly overfilled the material, which immediately collapsed after removing the flame from the burner. As the oxygen content in the gas mixture increased, the samples were exposed to fire. Initially, the flame appeared in the axis of the samples. In a short time, it spread horizontally in both directions towards the sample holder. As the flame front reached the metal frame supporting the sample, the fire went out. No significant smoke evolution or change in the incineration of the odor was observed. As the oxygen content in the gas mixture continued to increase, the flame behavior was similar, but the flame was larger and further propagation was observed: when the flame front reached the handle, the flame instead went out vertically downward, and then the material burned horizontally to the opposite end of the frame handle. The smoke produced in this case was larger, but still in relatively small quantities. There were no changes in the accompanying odor. At the spot where it reached the front of the flame, carbonaceous material could be seen on the thick layer of molten material. The LOI value in this case was considered the concentration at which the abovementioned fire behavior ended at least after reaching the prescribed distance or proceeded to burn the entire sample. Compositions with the highest LOI values for combustion samples perpendicular to the extrusion direction are PE/HAP and PE/FOS, for which the oxygen indices were 33.0% and 30.2%, respectively. Suitable compositions containing HAP and FOS from ASI exhibited less improvement in resistance to thermal degradation than those without ASI. (Table 5) Despite the reduction of the LOI for the PE/ASI composite, the improvement of this value relative to the pure PE sample was the smallest.

Due to the significantly different nature of combustion of the composite samples relative to the combustion of the reference sample, a second series of measurements was carried out in which the samples were burned in a direction parallel to the direction of their extrusion. The study started with a reference sample from pure PE. The starting point was the oxygen concentration in the gas mixture supplying the apparatus by 19.3%, which was the LOI value for the reference sample burned perpendicular to the film extrusion direction (Table 5). For the reference sample, the nature of the combustion in the second measurement series has not changed. At oxygen concentrations below the final LOI, the sample was slightly flushed and ignited after 1-2 seconds or ignited. At higher oxygen concentrations (going down to the limit value) the samples light up quickly, the yellow flame initiating in the axis of the test sample and propagating along it. Incineration of the material to the prescribed standard was carried out quickly, as did the in the case of the first measurement series. The amount of smoke, or smell, also did not change. The final LOI value was 19.6%, compared to 19.3% In the first measurement series there is no significant change taking into account the other location of the sample. For this series, in the case of composite samples, the nature of their combustion was similar to the combustion of the reference sample, as opposed to their behavior in the case of the first measurement series. As in the previously described cases, two types of behaviors of the composite samples tested were observed during the combustion test. In the absence of oxygen in the mixture with nitrogen flowing through the sample apparatus, they lit for a short time of about 1-2 seconds and then extinguished or did not deal with fire. As the oxygen concentration in the gas mixture increased, compositions containing additives burned in a similar way to the reference sample: after the burner was removed the flame appeared in the sample axis and its face moved vertically downwards. However, the difference in the course of the combustion process of the reference sample and the similarity to the combustion of composite samples in the earlier measurement series was the appearance of charcoal on the thickened, melting material. In the case of a test perpendicular to the extrusion axis, the molten material had an elongated shape and was located horizontally over the entire width of the burned section. In the case of a test carried out with parallel alignment of the sample to the extrusion axis, the scale was not so wide and concentrated in one place where the flame was previously located. In the course of the study, as it approached the concentration of oxygen in the gas mixture to the limit value but before reaching it, propagating in the abovementioned combustion method set before reaching the normalized distance. The smoke and odor remains unchanged. For the final LOI values of the individual composites (Table 5) and higher oxygen concentrations in the mix with the nitrogen supplied to the measuring device, the flame front exceeded the standard allowable combustion distance or the sample was completely burned. Analyzing the values collected for the second measurement series in Table 5 For the composite samples, a trend similar to that of the first series was observed: the addition of fillers in PE/HAP and PE/FOS compositions had the greatest impact on the improvement of the LOI value. The PE/ASI/FOS was slightly different from the trend with a LOI of 20.1%, which was exactly the same as for the PE/HAP composition (Table 5). In the case of PE/ASI compositions, a deterioration of the oxygen ratio was observed against the reference sample from pure PE. Causes of such a result were found in different thicknesses of prepared test samples. Measurement for this particular composition in a system parallel to the extrusion axis was repeated. The results obtained in the repeated study coincided with the results obtained initially.

3.3. Microcalorimetry of pyrolysis-combustion (MC)

Thanks to the micro-calorimetric assay, it was possible to obtain heat release rate (HRR) data for the compositions obtained as a function of time and temperature. The results in the form of HRR graphs as a function of temperature are shown in Figure 1. The maximum value of the heat relase rate (PHRR) for the reference sample was 1427 W/g at 493°C. This result was highest among the tested compositions, which meant that the addition of each of the applied fillers (and combinations thereof) had a favorable effect on the PHRR values of the individual composites. For the PE/FOS composition, the PHRR value was 1108 W/g at 496°C, an improvement of 22% over the reference sample. The PHRR for the PE/HAP composition was 872 W/g at 490°C. This is 39% better than the reference value. The reduction of the maximum heat transfer rate by 37% relative to the reference sample was noted for the PE/ASI composition with a PHRR of 900 W/g at 492°C. In the case of PE/ASI/FOS and PE/ASI/HAP compositions, the maximum heat generation rates were 1229 W/g at 495°C and 1199 W/g at 494°C. The simultaneous addition of colloidal silica and calcium phosphate reduced the PHRR of this composite by only 9% relative to the PE sample. In turn, the PE/ASI/HAP composite improved PHRR by only 16%.

By analyzing the course and shape of the obtained curves, it can be concluded that the differences in the time of heat generation for individual samples were insignificant. The resulting curves overlap practically throughout the measuring range. At a heating rate of 1°C/s, differences in heat generation did not exceed 5 seconds. The maximum position of the heat transfer rate as a function of time (and also the temperature) of the individual composite samples relative to the reference sample was not greater than 5 s.

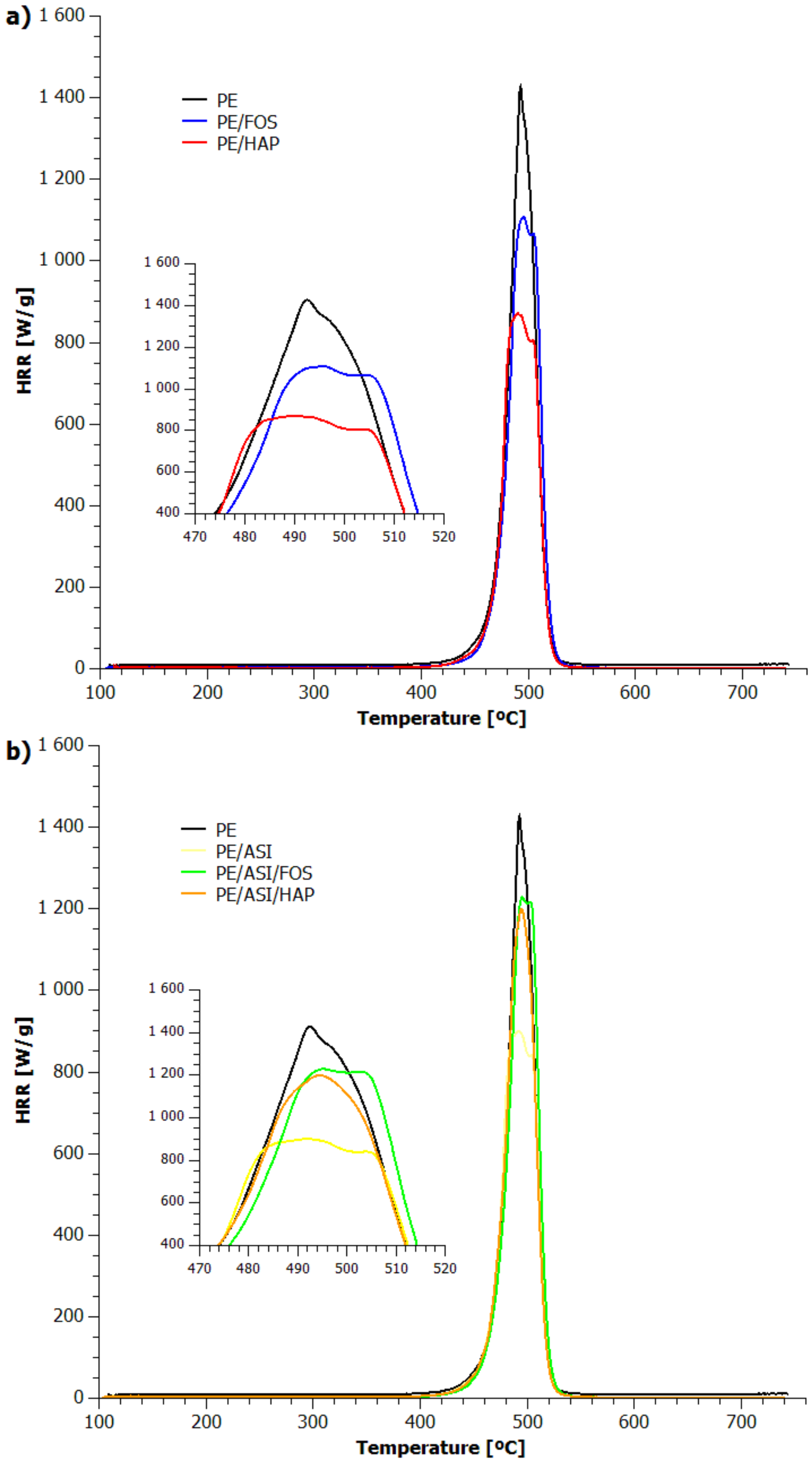

Figure 1. HRR graphs for a) polyethylene samples with calcium phosphate and hydroxyapatite and reference sample; b) PE/ASI composite samples

Based on the HRR graphs, the Total Heat Release THR values for the tested compositions were calculated for the test compositions which, when referring to the sample containing pure PE (assuming THR values for the PE sample as 100%), are shown in Figure 2.

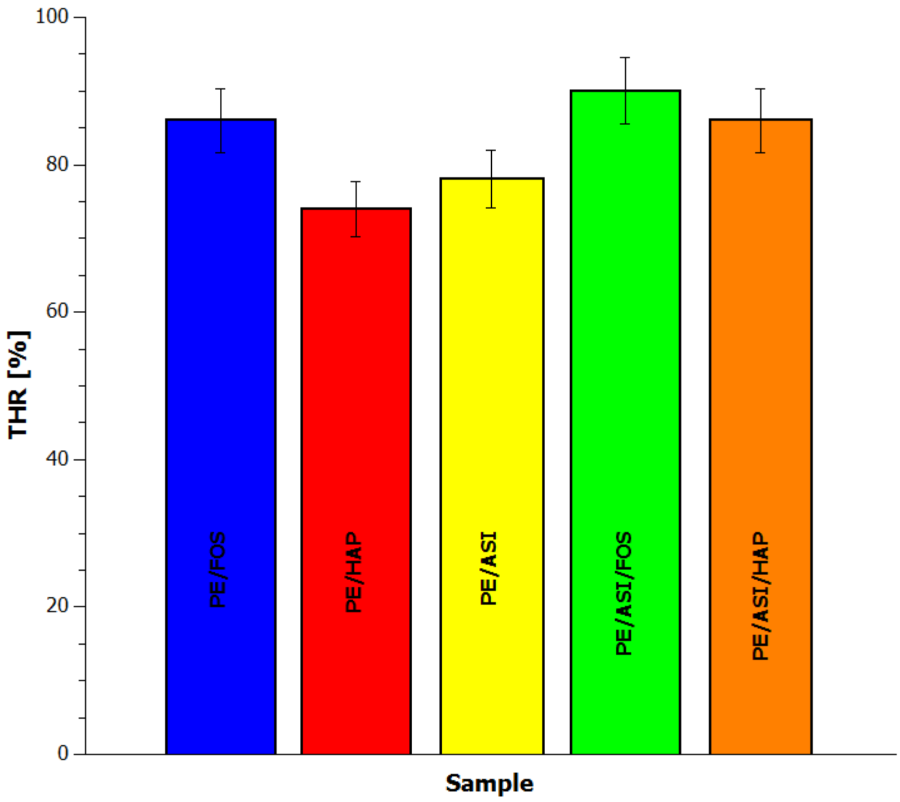

Figure 2. THR plot for obtained composites referenced to polyethylene sample.

By analyzing the values obtained, the thermal resistance was improved by 14% for PE/FOS and PE/ASI/HAP compared to the PE sample. The addition of hydroxyapatite improved the flammability of the resulting composite by 26% and colloidal silica by 22% (referring to the polyethylene sample). In the case of PE/ASI/FOS compositions, a flame retardant effect of 10% was achieved. The results obtained from the microcalorimetry test, calculated from the comparison of the PHRR and THR values of the reference sample with composite samples, are based on an equal trend.

3.4. Classification of the obtained films in terms of flammability

The classification of flammable films according to standard [4] has proved to be problematic. According to the above standard, the fire test can be carried out in a horizontal arrangement for self-supporting samples without the use of a suitable support or for non-self-supporting samples using a suitable support. The form and properties of the foils received prevented the UL-94 from being tested in a horizontal position. The test was performed in a vertical manner. The results are summarized in Table 4 and discussed in Section 3.1. In order to classify the tested flame retardants by comparing the observations and the results obtained with the relevant table in standard [4], it was found that it is not possible to assign any flammability class listed in standard [4] to any of the film obtained. The criterion causing the situation was the complete burning of each of the samples tested, up to the fixing element, which, according to standard [4], precludes the possibility of giving samples of any of the flammability classes.

According to [7] materials with an LOI value < 21% are classified as flammable materials LOI values ranging from 21-28% as flame retardant and materials with values LOI > 28% as non-flammable. Additionally, to classify material as self-extinguishing, its LOI value must be greater than 26%. Based on this distribution, all the test compositions obtained in the direction parallel to the extrusion axis of the film should be classified as flammable. as regards Examination in the direction perpendicular to the film extrusion axis, the test compositions shall be classified as follows: PE asphalts composition, PE/ASI and PE/ASI/FOS compositions as flammable, PE/ASI/HAP composition as flame retardant, self-extinguishing, PE/FOS and PE/HAP compositions are non-flammable - self-extinguishing.

4. Conclusions

After analyzing the flammability test results, it was found that the addition of applied fillers had a significant effect on the combustion mechanism. During the UL-94 flammability test, compositions with added fillers burned longer but slower, so that the rate of fire spread in the event of a fire would be less. An average of more detachable droplets of burning material spoke to the detriment of the additive compositions, as the burning droplet material could ignite other objects in the vicinity, as was the case with the cotton fabric during the test. The impossibility of classifying flammability to materials tested according to the UL-94 test would imply the need for further flammability tests. Performing additional tests according to standards, which described procedures would be better suited to testing foil materials, would probably allow for the classification of flammable materials to the appropriate classes. According to UL-94, the best fire retardant effect of polyethylene film was obtained by adding colloidal nanosilica. Then add calcium phosphate, which is used both as a single ingredient and in a silica composition. However, no synergistic effect exists between phosphorus compounds and silica, and there are no grounds for using them in such combinations as a mixture of flame retardants in composite material.

In the case of a study aimed at determining the oxygen ratio, a very important aspect influencing the result was the direction of the sample. The modified combustion mechanism and the form and size of the resulting charcoal in case of combustion of samples in a direction perpendicular to the axis of their extrusion may suggest specific orientation of the filler particles in the film during the extrusion process. Such specific placement of the filler particles can result in a significant flame retardancy effect of the test compositions. Hydroxyapatite and calcium phosphate supplements had the greatest positive effect. As with the UL-94 test, no synergistic effects were observed in PE/ASI/FOS or PE/ASI/HAP compositions. Attention should also be paid to the deterioration of the flammability of the PE/ASI composition tested in a direction parallel to the film extrusion axis. This behavior is confirmed only by the fact that the way of receiving the film and its arrangement during a fire can have a significant impact on the flammability.

The results obtained from the microcalorimetry test show the positive effect of the applied fillers on the reduction of the heat release rate. By ranking the effectiveness of the obtained compositions in terms of flame retardancy, whether based on PHRR or THR values, the classification is presented in the same way. The best effect was achieved for the PE/HAP composition. Subsequent flame retardancy is seen for PE/ASI and PE/FOS compositions. Despite improved flammability with reference PE, PE/ASI/HAP and PE/ASI/FOS showed an antagonistic effect - the effect of reduced flammability is worse than using individual fillers.

Taking into account the results of all studies, the most desirable flame retardant effect on PE was found by the PE/HAP composition. No synergistic effect exists between phosphorous compounds and silica, and there are no grounds for using them in such combinations as a mixture of flame retardants in a composite material.

Author Contributions: Tomasz M. Majka. conceived and designed the experiments; Piotr Stachak performed the experiments; Tomasz M. Majka and Piotr Stachak analyzed the data; Piotr Stachak wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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