INVESTIGATION INTO THE INFLUENCE OF FLAME RETARDANT ADDITIVES ON SOME FIRE PROPERTIES OF POLYESTER MATERIALS APPLYING SMALL-SCALE TESTING TECHNIQUES

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Abstract. In order to investigate the impact of some inorganic additive flame retardants on the selected fire properties of the materials based on polyester resin Polimal 1033 APy, small-scale fire testing techniques have been used. Seven samples have been studied: unmodified PES, PES modified with MoO_3 (7, 14 and 21 wt%) and PES modified with Sb_2O_3 (7, 14 and 21 wt%). The following flammable properties of materials have been determined: the heat of combustion (HOC), the ignition temperature of volatile thermal decomposition products (T_{ig}), self-ignition temperature and oxygen index. A cone calorimeter method has been used for determining heat release rate (HRR), mass loss, specific extinction area (SEA) and other combustion parameters. The toxicological analysis of combustion products has been conducted. Based on the obtained results, the following conclusions have been made: (1) MoO_3 and Sb_2O_3 added to the studied material change its flammable properties and fire parameters. It can be indicated by higher HOC, higher T_{ig} and self-ignition temperature, as well as by lower HRR and SEA. Modified materials become safer in terms of fire hazard. (2) A significant reduction in HRR_{max} of approx. 40% in the content of 7 wt% has been observed. The lowest HRR_{max} of approximately 300 kW/m^2 and 450 kW/m^2 have been obtained for 21 wt% in a range of 200–600 s at 30 kW/m^2 and 100–400 s at 50 kW/m^2 respectively. Except for a sample containing 7 wt% of Sb_2O_3, a clear local reduction in HRR (from 50 to 150 kW/m^2), in case of all modified samples has been noticed. (3) Sb_2O_3 has a greater impact on the thermostability of the studied materials compared to MoO_3 in all cases of heat flux density and additive concentrations. The effectiveness of Sb_2O_3, as a flame retardant is the most evident at 21 wt%.

Keywords: polyester materials; flame retardants; Polimal 1033 APy; small-scale fire testing; thermogravimetric analysis; flammable properties; cone calorimeter method; toxicological analysis.

Introduction

Polyester materials are of high significance among many types of materials applied nowadays in building engineering (building elements, division walls, glass roofs, structural elements, floor screeds). They are also used in textile industry, automotive industry, electronics, etc.

Traditional methods for reducing flammability are based on the modification of plastics by adding flame retardants, the so called *antipyrenes*, for example, as curing agents or fillers (Gałaj *et al.* 2012; Pofit Szczepańska, Półka 2002a, b, 2003; Półka 2001). Flame retardants inhibit the process of the thermal decomposition of the material subjected to thermal radiation resulting in a reduction in material combustion rate. A consequence of such process, among the others, is lower material flammability and a slower increase in fire temperature and CO concentration creating more favorable conditions for evacuation from the building. Basically, two mechanisms of acting antipyrenes, including physical and chemical, can be distinguished (Jankowska *et al.* 2007; Wilkie, Morgan 2009). The physical effect of the flame retardant agent mainly consists of the gas dilution phase and the formation of barrier layers that block the mass flow of thermal decomposition products and energy flow

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between gas and solid phases during material combustion. The chemical effect consists of antipyrene entering into free radical reactions of the combustion process in the gas phase and/or into reactions occurring in the solid phase.

A disadvantage of some flame retardants is frequently an increase in the toxicity degree of thermal decomposition products and the combustion of modified polymers in the fire environment. The products formed during combustion also pose danger to people during evacuation. Thus, due to the toxicity of the products of thermal decomposition and combustion, in recent years, the agents consisting of halogen atoms have been often substituted by halogen-free inhibitors.

A large number of papers present the analyzed results of different mechanisms for fire retardancy of polymer materials and small-scale fire tests using standard methods, such as a cone calorimeter, thermogravimetric analysis (TGA), limited oxygen index (LOI), a differential scanning calorimeter (DSC) and/or a vertical burning test (UL 94) (Carosio *et al.* 2012; Fukushima *et al.* 2010; Kandare *et al.* 2008; Kiliaris, Papaspyrides 2010; Konecki, Pólka 2006, 2009a, b; Laoutid *et al.* 2009; Li *et al.* 2012; Pan *et al.* 2012; Pereira *et al.* 2009; Pólka 2001; Seetapan *et al.* 2011; Tang *et al.* 2012; Tibiletti *et al.* 2011; Wei *et al.* 2011). The main directions of research in the considered field of the study include the determination of susceptibility to initiate combustion reactions, particularly under thermal and flow conditions simulating the 1st phase of fire, the quantitative and qualitative composition of thermal decomposition products reflecting smoke-generating capacity and the toxicity of the fire environment, the formation rate of critical heat flux during the combustion of epoxides enabling the transition of the 1st fire phase into the 2nd active phase, as well as the influence of the physical and chemical parameters of additives on the flammability of polyesters.

In order to investigate the behavior of polyester material based on Polimal 1033 Apy, the experimental part of the study on thermal and flammable properties looks at unmodified and modified inorganic additives during fire occurrence, as well as reveals heat release rates at the selected heat flux according to ISO 5660–1:2002 (Konecki, Pólka 2005; Pólka 2001). The toxicity of materials according to PN–88/B–02855 (1988) has been also investigated.

1. Subject of the study

For experimental small-scale studies by means of the cone calorimeter method, a trade name of polyester resin (PES) *Polimal 1033 APy* produced in the Chemical Plant *Organika Sarzyna* in Nowa Sarzyna, Poland and commonly applied in building engineering has been used. Structural resin has low viscosity and is medium elastic, orthophtalic and pre-accelerated. An abbreviation at the end of the name stands for

ecological, low styrene emission (letter A) and accelerated resin and does not require the use of cobalt accelerator (symbol Py). The basic parameters of resin are provided in Pólka (2001).

For modifying Polimal 1033 Apy resin, two inorganic oxides were used: antimony trioxide (Sb_2O_3) and molybdenum trioxide (MoO_3). The size of the mesh Sb_2O_3 (α) was up to 23 μm; however, MoO_3 made of 2–10 μm was produced by POCH S. A. Gliwice (Chemical Corporation in Poland). Modifications are aimed at enhancing fire resistance properties of resin. The quantities of added antipyrenes have been selected experimentally. Concentration range of additives depended on visible changes in a particular fire property of the lowest additive concentration and a lack of registered change in the same parameter of fire above the highest applied concentration of the additive. For selecting inorganic filler, a change in resin viscosity and gelation time was taken into account. The method of modification for both additives was the same. Both additives were added to polyester resin obtained as a result of polycondensation at a temperature of $t = 25$ °C and pressure $p = 0$ atm (Pólka 2001).

For small-scale studies, pure PES polyester and polyesters modified adding flame retardants reducing their flammability were used. The content of the additives in the modified samples was 7 wt%, 14 wt% and 21 wt%. Pure PES was transparent. The material with molybdenum addition was green, while a sample with the addition of antimony was white.

2. Test stand and measuring methods

The thermal analysis of unmodified and modified polyester materials was conducted in dynamic conditions. Thus, the mass of the studied decomposed sample was registered as a function of temperature at a constant heating rate. For thermogravimetric studies, the shredded samples of polyester material (of approx. 0.5 mm) made of unmodified Polimal 1033 Apy and modified with inorganic oxides having the mass of 140–170 mg were used. Thermal analysis was performed applying a derivatograph manufactured by Hungarian company MOM – Budapest (Magyar Optikai Muvek). The samples were placed in a thermoanalyzer oven and tested in the temperature range of 20–1000 °C at three different heating rates — 2.5, 5 and 10 °C/min. Analyses were conducted under atmospheric conditions.

In order to investigate the flammable properties of seven analyzed polyester materials, the following parameters were determined: combustion heat, the ignition temperature of volatile products of thermal decomposition, self-ignition temperature and oxygen indexes of the studied polyesters. The heats of combustion analysis were carried out based on PN–81/G–04523 (1981). The chosen method consisted of the complete combustion of the weighed sample of a
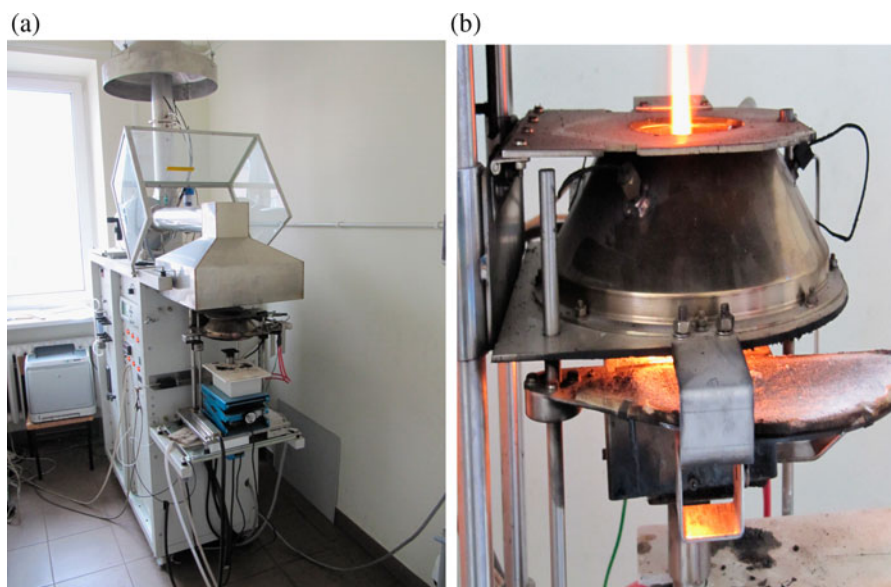
Fig. 1. General view of the cone calorimeter (a) and a burner with the sample after piloted ignition (b)

solid material in oxygen atmosphere under pressure in a bomb calorimeter and the measurement of temperature growth in water in the calorimetric vessel. For studying combustion heat, the samples of polyester products were used – shredded to the fraction of 1 mm of 1 g mass. The ignition temperature of the volatile products of thermal decomposition was determined according to PN–69/C–89022 (1969). The method consists of heating the sample up to temperature lower than 10 °C of the expected thermal decomposition temperature and testing the ignition (during 5 min) of emitted pyrolytic gases with reference to an auxiliary ignition source (most frequently flame). Polyester material samples shredded to the fraction of 0.5 mm (mass = 1 g) were placed in a metal thimble and put into an oven under constant temperature in the range of 150–400 °C. Self-ignition temperatures of unmodified samples and samples modified with inorganic oxides were determined based on the method described in ASTM D 1929–77 (1977). The method consists of placing the sample in the oven with adjustable temperature and measuring the lowest temperature of the oven walls at which the self-ignition of thermal decomposition products occur. This self-ignition temperature can be determined under both static and dynamic conditions. The dynamic method was applied (Stechkin apparatus CS–88 by Custom Scientific Instruments) in the presented studies more accurately reflecting fire conditions. The studies focused on the air conditioned samples of polyester material having the dimensions of 20×20 mm and the mass of 3 ± 0.5 g. The determination of oxygen indexes was conducted based on PN–76/C–89056 (1976) standard. The method of oxygen index consists of determining the lowest oxygen concentration in the oxygen and nitrogen mixture, at which a plastic sample fixed vertically in the measuring column burns for 3 minutes at a length of 5 cm. The samples of polyester materials with a shape of rectangular beams and dimensions of $80 \times 1 \times 4$ mm were tested employing standard test equipment manufactured by Stanton Redcroft.

For analyzing heat release rate and other combustion parameters, a cone calorimeter manufactured by Fire Testing Technology (Great Britain) was applied. Its general view is given in Fig. 1a. The tests were conducted according to ISO 5660–1:2002 standard. The samples of the studied polyester materials were subjected to the influence of the heat flux of 30 kW/m^2 and 50 kW/m^2. To select the power of heat radiation to determine fire parameters, a thermal flux simulating the 1st and 2nd phase of fire was used. Ignition was initiated by piloted ignition. The ignition of volatile products was performed by means of a spark igniter. The studies employed a horizontal placement of the tested samples with regards to the radiator (see Fig. 1b). Before testing, unmodified and modified polyester material samples having the dimensions of 100×100 mm were stored at 20 ± 2 °C, wrapped in aluminum foil and placed in the test frame for cone calorimeter studies. A surface of the samples subjected to heat flux impact was 88.4 cm^2, the thickness of the profiles was 4–5 mm, and the initial weight of the samples varied by a small percentage.

3. Studies on the results of thermal properties

The results of the thermal properties of polyester material samples are given in Table 1. The thermal distribution of the studied materials is a function of their composition and heating rate. Unmodified polyester in the range of the studied temperature

Table 1. Decomposition temperatures and mass loss of the studied polyester materials

Material	Heating rate (°C/min)	Initial tempera-ture of thermal decompo-sition (°C)	Tempera-ture of maximum mass loss (°C)	Maxi-mum mass loss (%)
Clear PES	2.5	165	260	75
	5	180	270	74
	10	180	270	73
PES + 7% MoO$_3$	2.5	185	290	69
	5	182	290	67
	10	182	291	66
PES + 14% MoO$_3$	2.5	195	300	70
	5	193	320	69
	10	193	300	70
PES + 21% MoO$_3$	2.5	192	300	46
	5	195	302	50
	10	195	312	51
PES + 7% Sb$_2$O$_3$	2.5	190	350	67
	5	180	290	74
	10	185	385	74
PES + 14% Sb$_2$O$_3$	2.5	180	340	62
	5	200	350	76
	10	210	380	69
PES + 21% Sb$_2$O$_3$	2.5	180	270	63
	5	200	360	58
	10	210	370	59

and at applied heating rates does not change its thermostability. The temperatures of starting thermal decomposition and maximum mass loss, influencing mainly the ignition temperatures of the studied materials vary slightly, which indicates that the variable heating rate of polyester material based on Polimal 1033 APy at the beginning of the 1st phase of fire, does not influence the rate of forming the fire environment. Modification with flame retardants such as molybdenum or antimony oxides has an impact on the thermostability of the material. The results of thermogravimetric studies shown in Table 1 indicate an inhibitive impact of both applied oxides, while significant effect has heating rate along with additive concentration. Taking into account three applied concentrations of additive – molybdenum trioxide (7, 14 and 21 wt%), a maximum increase in the decomposition temperatures of 30 °C was observed in the case of sample PES + 21% MoO$_3$ compared to unmodified polyester. For the maximum mass loss of the studied modified PES, the high concentration of the additive has a significant influence. At molybdenum trioxide content of 21 wt% found in PES, maximum mass loss decreases from 75 wt% (for unmodified PES) to 46 wt%, which significantly reduces the concentration of the flammable volatile phase and consequently reduces the risk of fire hazard posed by clear polyester material. In case of applying Sb$_2$O$_3$ as a modifier of PES flammability, changes in thermostability are more apparent. The thermostability of tested polyesters increases at all applied

concentrations of antimony trioxide and heating rates. The highest growth in both temperatures is that the beginning of thermal decomposition and maximum mass loss can be observed at Sb$_2$O$_3$ concentration of 14 wt% and the heating rate of 10 °C/min.

The maximum mass loss of the material based on Polimal 1033 APy has been demonstrated at Sb$_2$O$_3$ content of 21 wt% (59%). It should be noticed a significant variation of growth in the temperature of maximum mass loss at applied heating rates. An addition of antipyrenes increases the amount of resulting residues after pyrolysis. The highest amount of ashes after sample combustion can be observed in case of polyester material containing 21 wt% of MoO$_3$ and the heating rate of 2.5 °C/min. A comparative analysis of the influence of both tested additives on the studied polyester material, based on the obtained thermogravimetric results, demonstrated antimony trioxide to be a more effective modifier of the flammable properties of the products, based on Polimal 1033 APy rather than molybdenum trioxide increasing its thermostability.

4. Results and analysis of flammable properties

Table 2 presents ignition temperatures, the heat of combustion, as well as self-ignition and oxygen indexes obtained during testing the samples of polyester material. The flammable properties of the studied polyester material both modified and unmodified with flame retardants, were analyzed based on the obtained ignition temperatures of thermal decomposi-

Table 2. Ignition temperature, heat of combustion, self-ignition and oxygen indexes of the studied polyester materials

Material	Ignition tempe-rature (°C)	Heat of combu-stion (kJ/kg)	Self-ignition tempera-ture (°C)	Oxygen index (%)
Clear PES	308	26,636	380	17.2
PES + 7% MoO_3	310	23,855	391	18.9
PES + 14% MoO_3	314	22,780	410	19.0
PES + 21 MoO_3	320	20,726	418	19.1
PES + 7% Sb_2O_3	309	24,420	385	17.5
PES + 14% Sb_2O_3	310	23,165	397	18.2
PES + 21% Sb_2O_3	315	22,168	405	18.4

tion products, self-ignition temperatures, oxygen indexes and the heat of combustion. Three first values indicating the ability to initiate a combustion reaction listed above were determined applying standard methods using low-energy heat sources. The heat of combustion was determined employing the standard method of material combustion in oxygen. The obtained results of ignition temperature and self-ignition indicate that the impact of both additives on the flammability of the volatile phase, formed as a result of the thermal decomposition of PES, is insignificant taking into account the initiation of combustion that uses the MoO_3 modifier.

The maximum difference in the temperature values of ignition regarding unmodified and modified polyester material was 7 °C at 21 wt% content of molybdenum oxide in PES and 12 °C at 21 wt% content of antimony trioxide. In case of self-ignition temperatures of the studied materials, the maximum difference in the values of 38 °C has been observed for PES including 21% of Sb_2O_3 and 20 °C for PES with 21% of MoO_3. Most probably, in case of MoO_3, it is related to the low volatility of antipyrene, which, as demonstrated in further results, inhibits especially in the condensed phase slightly changing the composition of the volatile phase of the unmodified polyester material. Therefore, the values of both the temperature of the ignition of the volatile products of thermal decomposition and self-ignition temperature, before and after modification are similar. Greater effects of the differentiation of susceptibility for ignition have been demonstrated using Sb_2O_3, although antimony trioxide transits into the volatile state much easier, as a result of the thermal decomposition of polyester material, comparing to molybdenum trioxide. The obtained results indicate that the composition of the volatile phase formed during the thermal decomposition of the material modified with Sb_2O_3 has a lower ability of flame propagation either in the case of point heat source or heat radiation. The above observations have been also confirmed by the results of measuring the oxygen index (IO) of polyesters. However, mass and heat transfer are different during oxygen index measurements comparing to mass and heat transfer between heat source and material during studies on ignition and self-ignition temperatures. IO values vary insignificantly and thus the studied polyester both unmodified and modified can be still classified as easy to ignite (IO < 21%). Combustion heat values of the studied material with inorganic fillers are lower in comparison with the values for unmodified materials. Along with an increase in the concentrations of the applied oxides, combustion heat values are decreasing. The lowest value has been observed for resin containing 21 wt% of Sb_2O_3. As the effect of adding molybdenum and antimony trioxide and as the antipyrenes of polyester materials, the material made of Polimal 1033 Apy becomes safer in terms of fire hazard and reflects lower fire loading of the buildings in which polyester materials are used as building materials. The above feature allows applying the materials of a lower fire resistance in buildings.

5. Results and analysis of fire parameters and toxicity

One of the most important fire parameters and one of the main factors determining the rates of temperature growth and release of toxic products is heat release rate (HRR). The time when HRR reaches the maximum value is crucial; whereas the shorter the time, the greater is the risk for humans and the environment.

With reference to the conducted studies and applied software, the following fire characteristics and flammable properties of the material have been determined:

(1) Heat release rate in kW/m^2:
- Maximum heat release rate HRR_{max} in kW/m^2;
- Time for reaching $HRR_{max} - T_{HRRmax}$ in s;
- Mean heat release rate HRR_{mean} in kW/m^2;
(2) Mass loss rate MLR in $g/(m^2s)$:
- Mean mass loss rate MLR_{mean} in $g (m^2s)$;
(3) Total heat released THR in MJ/m^2;
(4) Effective heat of combustion HOC in MJ/kg:
- Mean effective heat of combustion HOC_{mean} in MJ/kg;
(5) Specific extinction area SEA in m^2/kg:
- Mean specific extinction area SEA_{mean} in m^2/kg;
(6) Final sample mass FSM in g;
(7) Time for constant ignition T_{ig} in s.

Table 3. Thermo-kinetic properties of polyester materials containing Polimal 1033 APy unmodified and modified with inorganic oxides under ignition conditions for the external heat flux of 30 kW/m^2 – Part 1

Material	HRR$_{max}$ kW/m^2	HRR$_{mean}$ kW/m^2	SEA$_{mean}$ m^2/kg	MLR$_{mean}$ g/(m^2·s)
Clear PES	685	340	856.1	24.2
PES + 7% MoO$_3$	413	244	909.9	16.6
PES + 14% MoO$_3$	361	204	858.6	16.3
PES + 21% MoO$_3$	279	164	952.6	14.3
PES + 7% Sb$_2$O$_3$	402	265	1048.5	17.9
PES + 14% Sb$_2$O$_3$	303	200	1068.4	14.4
PES + 21% Sb$_2$O$_3$	268	166	1017.5	16.4

The results of conducted studies in the form of selected thermo-physical and thermo-kinetic parameters of studied PES for two different external types of heat flux density – 30 and 50 kW/m^2 are shown in Tables 3–6. Figs 2–5 present HRR curves for pure and modified PES with pilot ignition at varying different heat flux density of 30 and 50kW/m^2.

Based on the conducted cone calorimeter studies, the following observations have been made:

(1) The addition of 7 wt% of MoO$_3$ and Sb$_2$O$_3$ to polyester material Polimal 1033 Apy reduces heat release rate for approx. 40–50% at the analyzed heat flux density (see Tables 3 and 5 and Figs 2–5);

(2) Along with an increase in filler concentration, HRR$_{max}$ and HRR$_{mean}$ of materials under conditions of ignition are decreasing thus reaching the lowest values of 21 wt% (see Tables 3 and 5);

(3) Anitmony trioxide more effectively reduces heat release rate from polyester material than molybdenum trioxide. HRR$_{max}$ values of the products containing Sb$_2$O$_3$ are lower for about 20% compared to the values of the products modified with MoO$_3$ under conditions of ignition and at the studied heat flux density (see Tables 3 and 5);

(4) Independently from MoO$_3$ concentration and heat flux density, HRR curves of

PES + MoO$_3$ have two peaks and a specific 'saddle', which indicates the formation of a carbonized layer on the surface of the material. The carbonized layer is a barrier for incoming oxygen and heat, and prevents the spread of the combustion process. The greatest difference in height between two peaks has been observed for PES + 7 wt% of MoO$_3$. HRR curves of polyester materials containing Sb$_2$O$_3$ are characterized by more stable HRR values compared to PES with MoO$_3$ in the whole combustion range. The above indicates a lack of the carbonized layer or the formation of a very small layer (see Figs 2–5);

(5) Along with an increase in the concentration of both flame retardants, heat release rate from modified PES is decreasing (see Tables 3 and 5 and Figs 2–5);

(6) Maximum HRR values and mean HRR values of unmodified and modified polyester materials based on Polimal 1033 Apy at the applied heat flux of 30 kW/m^2 are lower for about 40–50% compared to the values observed at the heat flux of 50 kW/m^2 (see Tables 3 and 5);

(7) Maximum heat release rates for unmodified and modified PES for applied heat flux density depend on the method of initiating the combustion process. The combustion theory distinguishes three types of combustion initiation: ignition, self-ignition and spontaneous combustion. Due to the fact that unmodified and modified polyester material does not undergo spontaneous combustion, the studies used two other types determining fire occurrence. Under conditions of self-ignition, HRR$_{max}$ values of the studied materials are lower comparing to the corresponding materials under conditions of the ignition of pyrolytic products. The difference in HRR$_{max}$ between materials arising from various types of the combustion initiation process is 14% at 30 kW/m^2 and 15–20% at 50 kW/m^2;

Table 4. Thermo-kinetic properties of polyester materials containing Polimal 1033 APy unmodified and modified with inorganic oxides under ignition conditions for the external heat flux of 30 kW/m^2 – Part 2

Material	T$_{ig}$ (s)	T$_{HRRmax}$ (s)	THR (MJ/m^2)
Clear PES	85	475	193
PES + 7% MoO$_3$	85	527	170
PES + 14% MoO$_3$	86	511	161
PES + 21% MoO$_3$	86	613	136
PES + 7% Sb$_2$O$_3$	95	408	173
PES + 14% Sb$_2$O$_3$	108	601	155
PES + 21% Sb$_2$O$_3$	108	275	129

Table 5. Thermokinetic properties of polyester materials containing Polimal 1033 APy unmodified and modified with inorganic oxides under ignition conditions for the external heat flux of 50 kW/m^2 – Part 1
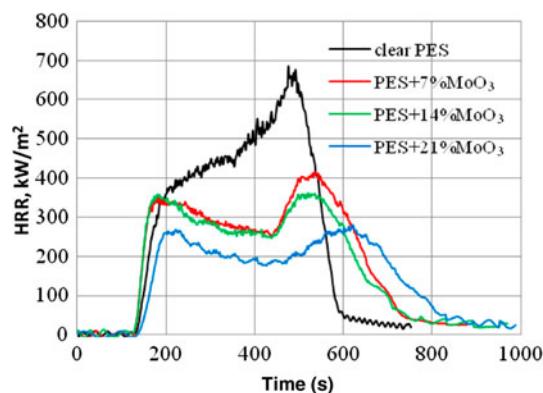
Material	HRR$_{max}$ kW/m^2	HRR$_{mean}$ kW/m^2	SEA$_{mean}$ m^2/kg	MLR$_{mean}$ g/(m^2 s)
Clear PES	1011	448	826.5	31.3
PES + 7% MoO$_3$	575	355	1090.4	22.0
PES + 14% MoO$_3$	564	344	1060.6	20.8
PES + 21% MoO$_3$	531	309	1118.7	18.5
PES + 7% Sb$_2$O$_3$	572	351	1121.0	24.4
PES + 14% Sb$_2$O$_3$	458	302	1160.1	20.6
PES + 21% Sb$_2$O$_3$	427	266	1099.3	19.2

(8) Time for the ignition and self-ignition of polyester materials modified with inorganic oxides are longer comparing to corresponding time for unmodified polyester. Together with an increase in the filler content of the material, the initiation of the reaction in the material becomes more difficult, while time for ignition and self-ignition becomes longer. Polyester material containing Sb$_2$O$_3$ is characterized by longer time for ignition and self-ignition comparing to time for PES with MoO$_3$. The greatest difference in time for ignition and self-ignition can be noticed in the results obtained at the heat flux of 30 kW/m^2 and conditions under the ignition of pyrolytic products. Molybdenum trioxide used as an additive for PES comparing to unmodified polyester, slightly extends time for ignition and self-ignition. Only in case of the material containing 21 wt% of MoO$_3$ under conditions of self-ignition and heat flux density of 30 kW/m^2, time for sample self-ignition is longer for 17% than time for the self-ignition of the unmodified material. Time for the ignition and self-ignition of the studied materials depends not only on the type and concentrations of fillers, but also on the heat release rate and type of combustion process initiation. At a lower heat flux of 30 kW/m^2, time for the ignition or self-ignition of the studied PESs is longer than at the flux of 50 kW/m^2 (see Tables 4 and 6);

(9) The application of the auxiliary ignition source (spark igniter) speeds up the ignition of a volatile mixture of the products of thermal decomposition with the air. At the heat flux of 30 kW/m^2 and under conditions of self-ignition, time for initiating the combustion process of materials is the longest;

(10) The influence of polyester material modified with inorganic oxides (MoO$_3$ and Sb$_2$O$_3$) can be also noticed, when analyzing the values of total heat released (THR) and mean effective heat of combustion (HOC), taking into account the mass loss rate of polyesters during combustion. Together with the increasing percentage content of oxides in the studied materials, the values of THR and HOC are decreasing; the impact of MoO$_3$ and Sb$_2$O$_3$ is similar (see Tables 4 and 6);

(11) The mean mass loss rates (MLR$_{mean}$) of the studied polyester materials under ignition and self-ignition conditions decrease along with an increase in the concentrations of the applied fillers. The highest value of MLR$_{mean}$ has been observed for unmodified PES. The thermal decomposition of cross-linked Polimal 1033 Apy including Sb$_2$O$_3$ proceeds faster than with MoO$_3$; it is indicated by higher values of MLR$_{mean}$ for materials containing Sb$_2$O$_3$ in the studied

Table 6. Thermokinetic properties of unmodified and modified polyester materials at the heat flux density of 50 kW/m^2 on piloted ignition – Part 2

Material	T$_{ig}$ (s)	T$_{HRRmax}$ (s)	THR (MJ/m^2)
Clear PES	40	343	198
PES + 7% MoO$_3$	40	383	204
PES + 14% MoO$_3$	40	99	197
PES + 21% MoO$_3$	40	98	189
PES + 7% Sb$_2$O$_3$	40	224	178
PES + 14% Sb$_2$O$_3$	40	389	164
PES + 21% Sb$_2$O$_3$	46	381	153

Fig. 2. Heat release rate for polyester material unmodified and modified with MoO$_3$ at the heat flux density of 30 kW/m^2 on piloted ignition

Fig. 3. Heat release rate for polyester material unmodified and modified with Sb_2O_3 at the heat flux density of 30 kW/m^2 on piloted ignition

Fig. 5. Heat release rate for polyester material unmodified and modified with Sb_2O_3 at the heat flux density of 50 kW/m^2 on piloted ignition
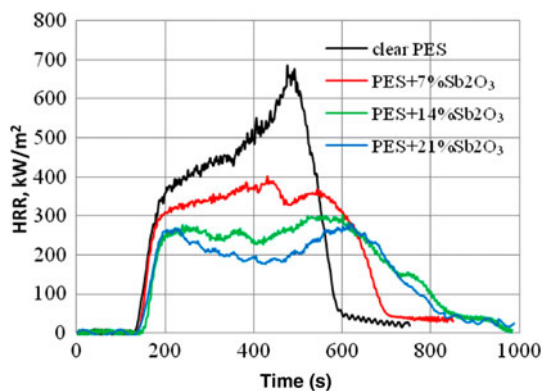
heat fluxes independently from the combustion initiation method. Considering the initial and final mass of the studied samples, it should be emphasized that, in most cases, residual mass after pyrolysis is larger for materials containing MoO_3. Investigated materials containing Sb_2O_3 under the influence of incident heat flux mostly demonstrate lower (comparing to the one containing MoO_3) ash content after combustion (see Tables 3 and 5);

(12) Flame retardants Sb_2O_3 and MoO_3 added to polyester resin increase the mean coefficient of the specific extinction area (SEA) of the material. The studied polyesters containing MoO_3 at the given heat flux and under ignition conditions demonstrate a lower SEA value of approx. 15% compared to the materials containing Sb_2O_3 (see Tables 3 and 5).

Studies on polyester resins have indicated that the additives do not have a significant influence on changes in toxicity. Toxicological profiles of concentrations for the studied substances with regards to
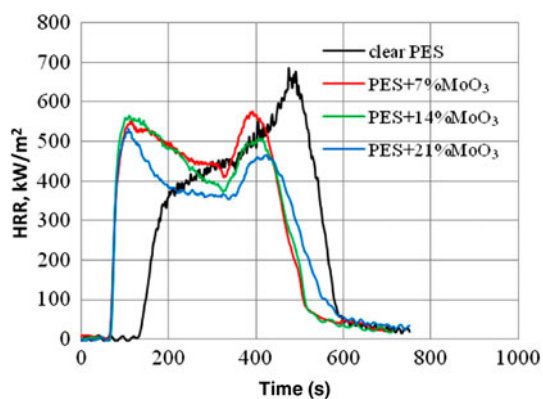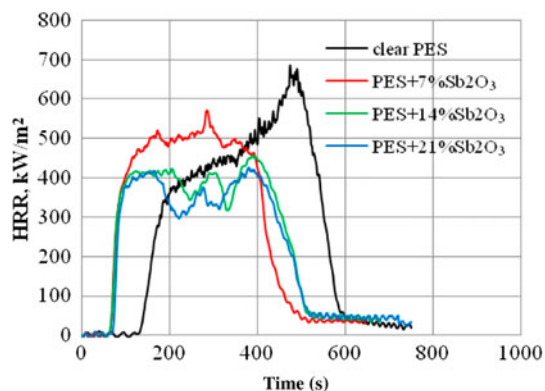
temperature allows noticing that along with temperature growth CO concentration drops and CO_2 increases. It has been shown that adding the antimony trioxide of 7 wt% results in a slight increase in toxicity, whereas in case of the sample consisting of 14 wt%, toxicity drops reaching the best result from all studied materials.

The main conclusion resulting from the analysis of the obtained results is that all studied materials were classified as moderately toxic thus being at the lowest safest limit according to PN–88/B–02855 (1988). The received results are presented in Tables 7–12.

Definitions of toxic indicators:

– toxic indicator W_{LC50} [g/m^3] – the weight of the given material, the decomposition or burning of which under testing conditions generated toxic threshold concentration of the given decomposition or burning product:

$$W_{LC50} = \frac{LC_{50}}{E}, \qquad (1)$$

where: LC_{50} [g/m^3] – threshold concentration of the given thermal decomposition product that causes the death of 50% of the population at an exposition of 30 minutes; E – specific emission [g/g] (mean arithmetical value of the specific emission value in view of the results of at least two tests);

Fig. 4. Heat release rate for polyester material unmodified and modified with MoO_3 at the heat flux density of 50 kW/m^2 on piloted ignition

Table 7. Toxicometric indicators of unmodified polyester material

Decomposition temperature (°C)	W_{LC50} (g/m^3)		W_{LC50M} (g/m^3)	W_{LC50SM} (g/m^3)
	CO	CO$_2$		
450	167.6	2231.2	155.9	93.3
550	92.4	1419.9	86.7	
750	88.6	64.0	37.1	

Table 8. Toxicometric indicators of modified polyester material $+7$ wt% Sb_2O_3

Decomposition temperature (°C)	W_{LC50} (g/m³)		W_{LC50M} (g/m³)	W_{LC50SM} (g/m³)
	CO	CO₂		
450	221.2	1610.5	194.5	86.9
550	40.9	448.9	37.5	
750	49.8	67.4	28.6	

– toxic indicator W_{LC50M} [g/m³] – the resultant of indicator W_{LC50} considering particular decomposition and burning products for the given temperature, delimited pursuant to the formula:

$$\frac{1}{W_{LC50M}} = \sum^{n} \frac{1}{W_{LC50}}, \qquad (2)$$

where: n – the number of determined products;
– toxic indicator W_{LC50SM} [g/m³] – the mean arithmetical value of indicators W_{LC50M} from particular temperature ranges (450 °C, 550 °C, 750 °C). W_{LC50SM} indicators are used for classifying materials:

$$W_{LC50SM} = \frac{W_{LC50M.450} + W_{LC50M.550} + W_{LC50M.750}}{3}.$$
$$(3)$$

Chemical decomposition and burning products according to PN–88/B–02855 (1988) are classified taking into account appropriate groups presented in Table 13.

Summary and general conclusions

The paper focuses on the results of small-scale studies considering the evaluation of the flammability of new polyester materials based on Polimal 1033 APy resin, in which special flame retardants, such as molybdenum and antimony trioxides found in different content (7 wt%, 14 wt% and 21 wt%) are used. The obtained results have been compared with data received from pure resin without any additives.

With reference to the analysis of the obtained results, the following conclusions have been formulated.

Table 9. Toxicometric indicators of modified polyester material $+14$ wt% Sb_2O_3

Decomposition temperature (°C)	W_{LC50} (g/m³)		W_{LC50M} (g/m³)	W_{LC50SM} (g/m³)
	CO	CO₂		
450	448.6	2790.3	371.5	139.6
550	35.7	535.6	33.5	
750	18.3	56.7	13.9	

Table 10. Toxicometric indicators of modified polyester material $+7$ wt% MoO_3

Decomposition temperature (°C)	W_{LC50} (g/m³)		W_{LC50M} (g/m³)	W_{LC50SM} (g/m³)
	CO	CO₂		
450	127.0	1797.5	118.6	56.3
550	38.1	544.1	35.6	
750	20.5	50.7	14.6	

Molybdenum and antimony trioxides introduced to polyester resin change the flammable properties and fire characteristic of the studied polyester material. Together with the increasing content of inorganic oxides, the modified materials based on Polimal 1033 APy become safer from the point of view of fire hazard. It is indicated by higher values of heat combustion, lower heat release rates of the modified materials under considered heat flux and in consequence of a lower fire load of the buildings, where structural elements are made of non-saturated polyester resins. Higher values of the ignition temperature of volatile products and self-ignition and time for ignition or self-ignition confirm the above conclusion, since polyester materials containing flame retardants MoO_3 and Sb_2O_3 inhibit the initiation of the combustion reaction, and thus inhibit fire development at its initial phase. An inhibitive impact of antimony trioxide on self-ignition and ignition temperatures and time for the self-ignition and ignition of PES is greater comparing the above temperatures and time for the material containing molybdenum trioxide. The effectiveness of Sb_2O_3 as antipyrene for polyester materials is the most evident when Sb_2O_3 concentration is 21 wt%. Antimony trioxide has a greater influence on the thermostability of the investigated material based on Polimal 1033 APy compared to molybdenum trioxide in all cases of heat flux density and all additive concentrations. There is a significant diversification of temperature growth in maximum mass loss in light of the studied heating rates, which indicates that the thermal decomposition of the studied polyester materials is a function of their composition and heating rate. The temperatures of the initial thermal decomposition of polyesters modified with oxides are higher compared to unmodified materials. The addition of inorganic fillers to PES

Table 11. Toxicometric indicators of modified polyester material $+14$ wt% MoO_3

Decomposition temperature (°C)	W_{LC50} (g/m³)		W_{LC50M} (g/m³)	W_{LC50SM} (g/m³)
	CO	CO₂		
450	158.4	1523.6	143.5	68.9
550	44.1	1025.6	42.2	
750	28.0	81.3	20.8	

Table 12. Toxicity classification of the thermal decomposition products and combustion of unmodified and modified polyester materials

Material	W_{LC50SM} (g/m^3)	Toxicity class
Clear PES	93.3	Moderately toxic
PES + 7% Sb$_2$O$_3$	86.9	
PES + 14% Sb$_2$O$_3$	139.6	
PES + 7% MoO$_3$	56.3	
PES + 14% MoO$_3$	68.9	

results in a growth in the temperatures of maximum mass loss during thermal decomposition and simultaneously in the increased amount of residues after pyrolysis. The mass of ashes obtained from polyester samples containing MoO$_3$ in view of the studied heat flux density is higher compared to unmodified materials and those containing Sb$_2$O$_3$ in considered concentrations.

The inhibitory effect of Sb$_2$O$_3$ on the studied material is related to both the condensed phase and the volatile phase. It is demonstrated by longer time for the ignition and self-ignition of the material consisting of Polimal 1033 Apy containing Sb$_2$O$_3$, compared to the material composed of MoO$_3$ clear PES at the heat flux density of 30 and 50kW/m^2. Antimony trioxide included in PES during the heating process shows greater tendency to transit into the volatile phase than molybdenum trioxide and indicates inhibiting time for ignition. Molybdenum trioxide applied in PES only slightly influences changes in time for the ignition or self-ignition of modified materials under studied conditions.

Toxicity studies resulting in the determination of toxicometric indicators have demonstrated that both unmodified and modified PES are moderately toxic. Therefore, the influence of additives on the toxicity of the studied materials is insignificant. However, it should be emphasized that the lowest toxicity among all introduced samples ($W_{LC50SM} = 139.6$ g/m^3) was observed in PES containing 14 wt% of antimony trioxide.

The applied flame retardants even at the concentration of 7 wt% cause a significant reduction in heat release rate for approx. 40% (from 700 kW/m^2 to 400 kW/^{2}). A further increase in the content of additives, though to a lesser degree of approx. 30%, further decreases HRR values. The lowest HRR$_{max}$ values of about 300 kW/m^2 at the heat flux of 30 kW/m^2

Table 13. Toxic properties of decomposition and burning products of materials

W_{LC50SM}	Toxic properties of decomposition and burning products of materials
≤15	Very toxic
>15, ≤40	Toxic
>40	Moderately toxic

and 450 kW/m^2 and the radiation source of 50 kW/m^2 were obtained in the concentration of 21 wt%.

In the range of 200–600 s at 30 kW/m^2 and 100–400 s at 50 kW/m^2, with the exception of the sample containing 7 wt% of Sb$_2$O$_3$, a visible local reduction in heat release rate in case of all modified samples (from 50 to 150 kW/m^2) can be observed and indicates the formation of the carbonated zone on the surface, which is a barrier to incoming oxygen and heat, thus reducing flame propagation.

During combustion initiated by spark ignition in case of the sample with no additives, heat release rate constantly increases very rapidly in the first phase and slows down up to the maximum value within next 200 s. In case of the samples containing additives, after approximately 200 s for 30 kW/m^2 and after 100 s for 50 kW/m^2 and following a rapid increase in HRR, the value stabilizes approximately at the level of 250 kW/m^2 at the heat flux of 30 kW/m^2 or at the level of 300–400 kW/m^2 at the heat flux of 50 kW/m^2, and, in most cases, forms a specific 'saddle'.

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