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Flame-Retardant Unsaturated Polyester Resins: An Overview of Past and Recent Developments

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Additional information is available at the end of the chapter

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Abstract

The chapter presents a positive effect of reduced flammability of thermoset resins, thanks to the use of halogen-free flame retardants (FRs) and multi-ingredient modifiers that combine conventional phosphorous/nitrogen additives interacting with nanofillers. The impact of these inhibitors on the level of flammability of polyester polymer compositions was defined by determining the value of limiting oxygen index (LOI), thermogravimetric analysis and cone calorimeter (CC) analysis of thermal destruction processes. Morphology of composites was assessed by scanning electron microscope and analysis of actual SEM micro-graphic images. The analysis of thermal decomposition of the materials under examination confirmed flammability-reducing properties of the hybrid flame retardants used, and a synergy effect was observed between conventional modifiers and nanofillers, specifically expandable graphite and synthetic precipitated silica. The multi-ingredient composition of flame retardants turned out to make significant progress in achieving the desired level of flammability in polyester resins. Nanocomposites are a new class of polymer systems.

Keywords: flame retardancy, halogen-free antipyrine, nanofillers, nanocomposites, flame retardants, polyester resins

1. Introduction

Unsaturated polyester resins are the most commonly used thermoset resins in the world. More than 2 million tonnes of unsaturated polyester resins are utilized globally for the manufacture of wide assortment of product, including pipe, tanks, sanitary ware and high-performance components for the building, marine, electric and automotive industries. High thermal and heat stability, low shrinkage and excellent mechanical properties are typical for their polymers. Those applications in addition to the mechanical and electrical properties also require good flame retardants of the materials.

The contemporary chemistry of polymers and polymeric materials faces extraordinarily high requirements as regards broadly understood ecology of production processes and product properties, including reduced flammability and lower emission of toxic compounds generated as a result of thermal destruction of polymer materials.

This applies mainly to structural polymer materials that we encounter in daily life (construction, transport, household accessories and sports articles).

One of the commonly and broadly used groups of structural polymers comprises specifically unsaturated polyester and epoxy resins. Therefore, the problem of suppressing flammability of polyester and epoxy resins is currently one of the most serious and at the same time most difficult challenges for the state-of-the-art technologies for the production of these materials.

While burning, unsaturated polyester resins and polyester glass laminates made with these resins give off significant quantities of thick black smoke. This phenomenon is accompanied by the emission of toxic gases (HCl, HBr, CO), especially if flame-retardant halogen polyester resins have been used. Rescue operations become harder or even impossible.

Therefore, it is important that polyester resins are obtained that do not sustain the burning process, characterized at the same time by an appropriate level of flame retardancy and reduced emission of smoke.

Reducing flammability of thermoset materials by the addition of halogen compounds or inclusion in the structure of these polymers of a chemically bound halogen has been discontinued on a successive basis for ecological reasons. These compounds, even though they are very effective in decreasing flammability of thermoset materials and show favorable synergy effect, mainly in the halogen-antimony system, are characterized by the emission of toxic products in combustion, mainly hydrogen chloride and hydrogen bromide. Their strong corrosive and irritant action, resulting from the use of aromatic bromine compounds, is a reason for limiting the use of this method and searching for alternative solutions. Undertaken activities refer to official drafts, laws and legal recommendations. In the territory of the European Union, the REACH Regulation (with supplementary appendices) of the European Parliament and the Council has been in force since 2007, as the regulation for managing chemical policy in EU states [1]. The main objective of REACH is to control introduction of and transactions in already marketed chemical compounds in terms of safety of human health and life and natural environment. One of the major elements of legislative regulations (EU REACH regulation) is to assess especially controversial substances and to gradually withdraw them from the EU markets. In addition to REACH, EU states are also bound by the RoHS Directive, which includes a ban on using halogen derivatives in the production of electronic and electric equipment. Most conventional flame retardants like halogenated organics have been limited in their utility due to peoples' health and environmental concerns, and other fire retardants like aluminum hydrates (ATH) are expensive and need to be used in large quantities which the thermoset polymers lose its original mechanical properties. The application of ATH or magnesium hydroxide requires a very high loading of the filler within the polymer matrix. Loading levels of more than 60 wt.% are necessary to achieve a suitable flame retardancy. The disadvantages of these loading levels are high density and lack of flexibility of the final products, as well as low strength properties and problem in extrusion/compounding technical process.

These legislative initiatives are a part of justified attempts and a necessity of searching for new, equally effective methods of reducing flammability of thermoset materials. Currently, reducing flammability of these polymers focuses on the use of halogen-free inorganic compounds, which, as additive modifiers, do not form chemical bonds with a polymer. From an industrial practice perspective, it is important that the desired flammability level is achieved at the lowest possible concentration of a flame retardant (FR) [2]. Therefore, the current tendency among academic institutions is to focus on the use of multi-ingredient halogen-free FR systems, taking advantage of the synergy effect of their action [3]. Synergy effects should be considered one of the most important phenomena related to the issues involving retardation of polymer flammability.

Recently, increased interest in to the use of additions in the form of nanocompounds as modifiers of multiple properties of polymers, including their thermal stability and fire resistance. Large interfacial surface and nanometric dimensions of modifier particles differentiate nanocomposites from traditional composites in a significant way. Nanocomposites avoid the disadvantages of these conventional flame-retardant systems. Therefore, the assumption that nanomaterials formed this way make it possible to achieve significant progress and benefits for human kind and natural environment due to their distinctive properties compared to the properties demonstrated by macrometric size particles has also rolled out to the issue of effective reduction in flammability of nanocomposite materials [5–7, 14].

To produce polymer nanocomposites, including polyester ones, natural layered aluminum silicates are usually used, such as smectites, kaolinites, halloysite nanotubes, including mainly montmorillonite (MMT), or modified compounds—by ionic exchange of MMT-based clay with quaternary ammonium salts. Layered silicates dispersed in a polymer matrix are the most popular form of hybrid nanocomposites [16, 17]. Commonly used MMT-modifying ammonium salts, which contain long alkyl carbon chains in their structure, make aluminum silicates acquire organophilic properties, improve their affinity to a polymer matrix and thus reinforce composites' thermal stability which is determined by the length, number and saturation degree of alkyl chains. Nanocomposites modified this way demonstrate better thermal resistance, lower flammability and advantageous strength properties [13]. This concerns, however, mainly nanocomposites obtained with the use of polyolefines, polyamide, polystyrene [9–11], PVC [12] and other thermoplastics and elastomers, such as rubbers—SBR, BR and HNBR [4, 5, 8].

The results of experiments conducted in recent years on thermoset materials with modifications by mere MMT or organophilic MMT (oMMT) have confirmed a positive impact of this modification on strength properties, including mainly a significant increase in Young modulus of the products, but at the same time it has turned out that their flammability reducing effect is less favorable [18, 19].

The analysis confirms these observations and suggests a reason for this phenomenon. An effective multi-ingredient system has been proposed, which combines the joint effect of conventional flame retardants and selected nanocompounds, including expandable graphite and synthetic precipitated nanosilica [20]. The silica used in the experiments is a synthetic silicon oxide obtained by acidifying sodium silicate with sulfuric acid. In order to improve compatibility of silica and polymer matrix, acidification process was modified to obtain a suspension

of precipitated silica, and then, this suspension sustained separation and drying processes. The resultant silica in the form of spheroid pearls was pulverized or subjected to wet granulation. It should be noted that precipitated silica contains a number of silanol groups, which do have a positive impact on interaction with a polymer, but they also lead to reinforcement of hydrophilic properties. Therefore, in the course of analysis, modification of silica with pro-adhesive compounds was suggested, such as silane and borate titanate compounds. Control of these parameters, combined with the control of pH, temperature, reaction duration, and molar ratio of reagents, makes it possible to obtain a portfolio of products from the group of nanosilica modifiers. In this analysis, nanosilica of the optimum set of properties was used, said properties being a sign of a possibility to obtain nanocomposites characterized by favorable thermal stability and lower flammability.

In order to reinforce flame retardation effect by the use of mere nanocompounds, polyphosphoric polymers were mainly used, intumescent flame retardants (IFR) in the form of melamine polyphosphate, ammonium polyphosphate and melamine borate, showing a proven effectiveness in inhibiting the flame. In this process, benefits of phosphoric-nitrogen flame retardants were realized, showing a synergy effect in reducing heat release rate (HRR) and positive effects in the reduction of flammability of structural compounds while using boron compounds [15, 21, 22].

An important part of the work, consistent with the authors' intent, refers to taking advantage of the benefits of using hybrid flame retardants, combining phosphorous-derived modifiers of thermoset materials' combustion process with selected modifiers when compared to the effect of reducing flammability level by using a single ingredient of the system only [23, 24]. In the course of experiments, optimum recipes and technological parameters for obtaining composite thermoset resins (unsaturated polyester resins and epoxy resins) with the use of multi-ingredient flame retardants were investigated. It was suggested which mechanism to use and how a deliberately chosen selection of multi-ingredient FR modifiers can have a positive impact on flame inhibition and lower smoke emissions.

2. Experiments

2.1. Materials and raw materials

Polimal 103A—structural orthophthalic unsaturated polyester resin, produced by Zakłady Chemiczne "Organika-Sarzyn" CIECH S.A. Viscosity in the range of 300–500 mPa.s, styrene content of 35% (UP₁) or equivalent orthophthalic polyester resin, DION 9500 Series produced by Reichhold, Inc. Company (UP₂).

Hardening system: two parts by weight of methyl-keton hydrogen peroxide Luperox K-1 and 0.4 parts by weight of cobalt naphthenate (1% Co).

Zinc borate: ZnO B₂O₃·2H₂O (ZnB)—commercial name of the product Flamtard Z-10 is product of Waardals Comp.

Zinc stannate/hydroxy zinc stannate: ZnSnO₃/ZnSn(OH)₆ (Zn/Sn)—commercial name of product Flamtard S/Flamtard HB1 was produced by Alcan Chemical Europe.

Melamine polyphosphate(MPP): crystalline form of P_2O_5 content = 32–33% and N = 41–42%, average grain size of 2–3 μm , was manufactured by Zakłady Chemiczne” Alwernia” S.A.

Ammonium polyphosphate (APP) was manufactured by Clariant GmbH, commercial name of the product: AP 412.

Melamine borate (MB): experimental product of the Institute of New Chemical Synthesis is branch of the Institute of Inorganic Chemistry in Gliwice.

Montmorillonite (MMT) and MMT modified with quaternary ammonium salts (oMMT) was manufactured by Southern Clay Products, commercial name of the product: Nanofil 5.

Expandable graphite: EG 096 (EG) was manufactured by Synograp S.A.

Synthetic precipitated silica ($n\text{SiO}_2$): experimental product of the Institute of New Chemical Synthesis is branch of the Institute of Inorganic Chemistry in Gliwice.

2.2. Method of obtaining flame-retardant polyester compositions

For technical reasons, it was decided to introduce all flame retardants into ready-made polyester resins before the addition of hardening agents. Thanks to this procedure, it was possible to modify different types of resins in practice, at both resin manufacturers and processing entities. Additions were stirred in using a low rotation speed mixer per approx. 5 min. After first stirring with a low speed rotation mixer, the process was continued in an ultrasonic mixer provided with a turbine mixer (approx. 4500 rev/min). Resultant compositions were additionally ground in a high rotation speed homogenizer Mixman Comp., especially if nano-compounds were used in a composition. It was a guarantee of obtaining a stable and homogeneous composition of resins with flame retardants after approx. 80–90 min of stirring.

2.3. Testing methodology

2.3.1. Limiting oxygen index

Following industrial practice, measurements of limiting oxygen index (LOI) were used as a preliminary indication of relative flammability, said index representing mainly the level of flammability of volatile products of polymer decomposition. Measurement of LOI carried out to the standard PN-EN ISO 4589–2:1999/A1:2006 [25].

2.3.2. Thermogravimetric analysis

Thermogravimetric analysis was performed using a thermogravimetric analyzer TGA/SDTA 851 device by Metter Toledo. Samples of 10 g were placed in platinum melting pots with the capacity of 150 g. Heating up progressed in defined cycles, namely within the range of 25–800°C in air or nitrogen atmosphere and with a heating rate of 20°C/min.

2.3.3. Cone calorimeter tests

In the presented work, tests were performed using a British cone calorimeter FTT Dual Analysis Cone Calorimeter. Using computer analysis, a number of flammability properties

of materials were defined in line according to ISO 5660:2002 [26], part 1 “Reaction to fire tests – head release rate, smoke production and mass loss rate” using an external heat stream of a density of 25 or 50 kW/m² and air flow rate of 24 l/s. Type of burning reaction initiation-ignition was with a horizontal orientation of samples relative to a radiator. A spark fuse was used to ignite gases. Frequency of data compilation was 5 s for each.

Tests were performed on previously air-conditioned samples, 100 × 100 × 10 mm, having constant relative moisture and constant mass.

2.3.4. SEM tests

SEM tests were performed using a scanning electron microscope Hitachi SU8010. Tests were performed on specimen sections of sample test blocks and hardened resin composites after their modification.

SEM tests were also used to analyze the surface of tested composites after charring as a result of cone calorimeter tests.

3. Results overview

3.1. Halogenated unsaturated polyester resins

Halogenated unsaturated polyester resins are produced mainly on the basis of HET acid (hexachloroendomethylenetetrahydrophthalic acid), obtained by reacting maleic anhydride with hexachlorocyclopentadiene. Polyesters based on this acid do still have industrial importance and continue to be used in polyester resins produced by European and American companies, like Ashland Groups HETRON among others.

The production of HET acid-based polyester resins was also launched in Poland at the beginning of 1960s. The trade name of the product was Polimal 162, and it was widely used for the construction of flame-retardant rescue boats. The production of a new type of an unsaturated polyester resin with HET acid, characterized by better chemical resistance, was restored in the Chemical Plant “Organika-Sarżyna” in 1997.

Hooker Chemical Co. launched the process of chlorinating phthalic anhydride to tetrachlorophthalic acid anhydride, and Michigan Chemical was brominated phthalic anhydride to tetrabromophthalic acid anhydride. Tetrahalogenphthalic compounds were a basis for several flame-retardant unsaturated polyester resins launched at the turn of 1960s and 1970s. In the same period, attempts were made to favorably introduce bromine into a polyester chain by the use of brominated dioles (e.g., dibromoneopentyl glycol) or direct use of elementary bromine. What should be also mentioned is the use of tetrabromobisphenol A, which became a basis for the launch of several types of unsaturated polyester resins, type Derakane, characterized by good resistance to thermal shock and particularly favorable resistance to corrosion. Another method of introducing bromine atoms into a resin structure, mainly in the case of vinyl-ester resins, is the use of brominated cross-linking agent, such as dibromostyrene.

However, one should note that halogenated unsaturated polyesters can be obtained not only by polycondensation of dicarboxylic acids and (maleic, phthalic) acid anhydrides with glycols, but also by copolymerization of acid anhydrides with epoxy compounds, for example, 1,1,1-trichloro-2,3-epoxypropane or epichlorohydrin. Thus, chlorinated polyester resins with reduced flammability was obtained. An additional advantage of the technology is that it is waste free. One of the first industrial products obtained by catalytic addition of epichlorohydrin to dicarboxylic acid anhydrides, which we describe in detail in the next section of this resume, was Polimal 160 produced by the Chemical Plant "Organika-Sarzyna"-CIECH.

3.2. Halogen-free flame-retardant modifiers in polyester resins.

3.2.1. Modification of resins by using tin-zinc compounds

In 2003, we started experiments on the reduction of flammability of polyester resins using tin and zinc compounds. For experiments, we used oxides and hydroxides of these metals, which constituted a new group of halogen-free flame retarders relative to thermosetting resins. The results obtained by experiments make the flame retarding efficiency of these compounds more specific compared to the existing commonly used flame and smoke suppressant, that is, antimony trioxide (Sb_2O_3).

The experiments with the new compounds led to the following conclusions:

1. Compared to the experiments testing thermal degradation of unsaturated polyester resins modified with $\text{ZnSn}(\text{OH})_6$, we concluded that thermal decomposition proceeded in a complex way consisting in the precipitation of a series of low-molecular products coming from the decomposition of structures containing phthalic anhydride, and then, at higher temperatures, styrene, benzoic acid and other aromas. The analysis of the decomposition process for the samples modified with Sn/Zn indicates that the intensity of CO_2 emission was much reduced, and at the further decomposition stage, trace amounts of water and HBr occurred. Based on the experiment results, we proposed a thermal decomposition mechanism for modified unsaturated polyester resins of reduced flammability.
2. Following the actual kinetic analysis of the thermal decomposition process, we found that an unsaturated polyester resin decomposed in three stages. The first one was characterized by the activation energy of around 130 kJ/mol, comparable to depolymerization energy of polymerized polystyrene. The second stage, with activation energy of 150–170 kJ/mol, could be attributed to the decomposition of a cross-linked polyester network, wherein the third stage ($E > 200$ kJ/mol) was random macro-chain decomposition, leading to the formation of low molecular decomposition products. For a sample modified with $\text{ZnSn}(\text{OH})_6$, we concluded that introduction of an addition leads to an increase in (apparent) activation energy for the area of $\alpha > 0.8$. The kinetic analysis by nonlinear regression showed that for a nonmodified polyester resin, the best statistic distribution (F-test) corresponded to the Avrami-Erofeev (nuclei growth) model, and for polyester compositions modified with $\text{ZnSn}(\text{OH})_6$, the best distribution was for the n-th order autocatalytic reaction.

3. Stabilizing impact of $\text{ZnSn}(\text{OH})_6$ can be explained by the formation of a spheroid surface barrier blocking or inhibiting the heat flow from the decomposition zone to the substrate and by reacting tin compounds with radical decomposition products of a high-molecular compound.
4. When it comes to the choice of the most effective examination of resins reflecting their behavior in a fire in the most reliable way, we chose the experiments performed with the use of a cone calorimeter according to ISO 5660: 2002. The analysis of the combustion process of polyester compositions conducted with the cone calorimeter method, being the state-of-the-art and primary method of examining polymers' flammability, let me conclude that the presence of Sn/Zn flame retarder led to the reduction in the heat release rate and total heat release, significant reduction in smoke emission and longer time required for the ignition of the composition.
5. The results are illustrated by the following curves and diagrams presenting the selected figures (**Figures 1–4**) of the analysis of composition processes for polyester composites modified with antflammable Sn/Zn in juxtaposition with analogically prepared samples of nonmodified polyesters. The experiments were done at heat output of 25–50 kW/m^2 .

Analysis of the thermoanalytical experiments and combustion process was a basis for the proposal of the $\text{ZnSn}(\text{OH})_6$ thermal stability mechanism for unsaturated polyester resins:

UPR/UP \rightarrow phthalic anhydride, styrene, aromas + $\text{R-CH}_2\text{-Br}$,

where R – hydrocarbon chain,

$\text{R-CH}_2\text{-Br} + [\text{ZnSn}(\text{OH})_6] \rightarrow \text{ZnSnO}_3 + \text{H}_2\text{O}] \rightarrow \text{Zn}_2\text{SnO}_6 + \text{SnBr}\chi + \text{hydrocarbons}$,

where: $\chi = 2$ or 4.

$\text{SnBr}_2 + \text{H}_2\text{O} \rightarrow (\text{SnO}, \text{SnO}_2) + \text{HBr}$.

Resultant hydrogen bromide acts as a radical “catcher.”

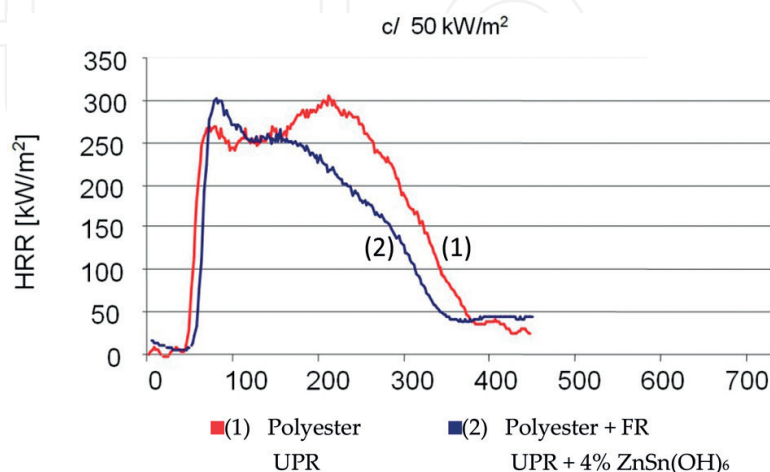


Figure 1. Heat release rate (HRR) at heat exposure of 50 kW/m^2 .

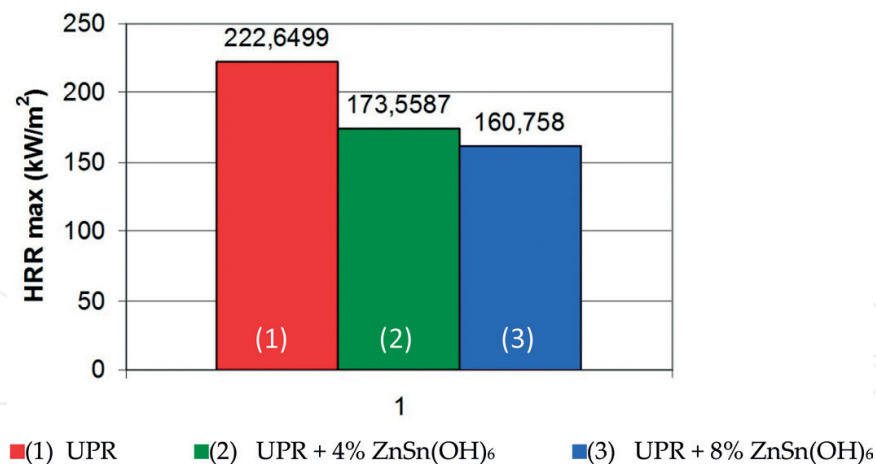


Figure 2. Maximum heat release rate (HRR max).

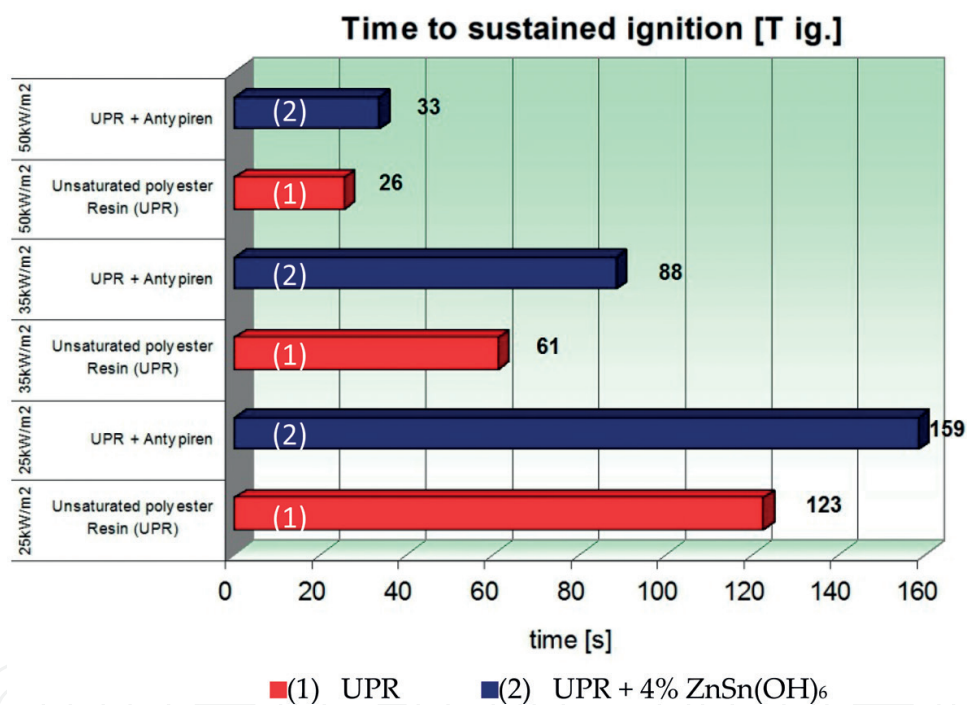
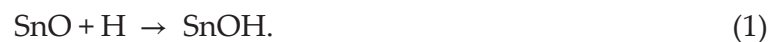


Figure 3. Time to sustained ignition (T ig) at different heat exposures of 25–50 kW/m².

It can also be assumed that H, OH and RO radicals formed as a result of unsaturated polyester resin bond decomposition can take part in the reactions with SnO and SnOH:





The aforesaid reactions form the so-called catalytic cycle.

The aforesaid findings confirm the suggestions related to the effective action of $\text{ZnSn}(\text{OH})_6$ as a flame-retardant agent stabilizing unsaturated polyester resins in the conditions of a fire risk.

3.2.2. Use of boron compounds as flame retarders for unsaturated polyester resins

A logical addition to the abovementioned scope of experiments focusing on the reduction of flammability of polyester resins was my concept to use boron compounds and boron salts as FR modifiers. We took an assumption that instead of the known antimony oxides cooperating with a halogen embedded in a polyester chain, one of zinc borate forms could be used, namely $\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. It turned out to be an effective flame retarder for the majority of halogen unsaturated polyester resins, specifically for those, for which chlorine or bromine atoms were bonded with aliphatic or cycloaliphatic and not aromatic fragments of a molecule. The results of these experiments made us check the effects of modifying the selected unsaturated resins with the new halogen-free and additionally physiologically neutral flame retarders in the form of boron compounds. For the experiments, we used the following compounds: anhydrous boric acid of a special physical and chemical structure, zinc borate, calcium borate, ammonium pentaborate, boron trioxide, boron phosphate and melamine borate. The new boric flame retarders turned out to be more effective than zinc borate used so far. We achieved the best results using melamine borate. As for the other FR additions, ammonium pentaborate and boric acid/ammonium polyphosphate system are worth mentioning. As all of the most effective modifiers contain both boron and nitrogen atoms in a molecule, we could assume the synergy action of these elements.

The analysis of the pyrolysis process of polyester compositions modified with boron compounds confirmed—as suggested in the body of literature—the generation of a high temperature of boric acid and formation of a foamy protective layer on the composition surface, limiting or even stopping the process of a product's burning. While using melamine borate,

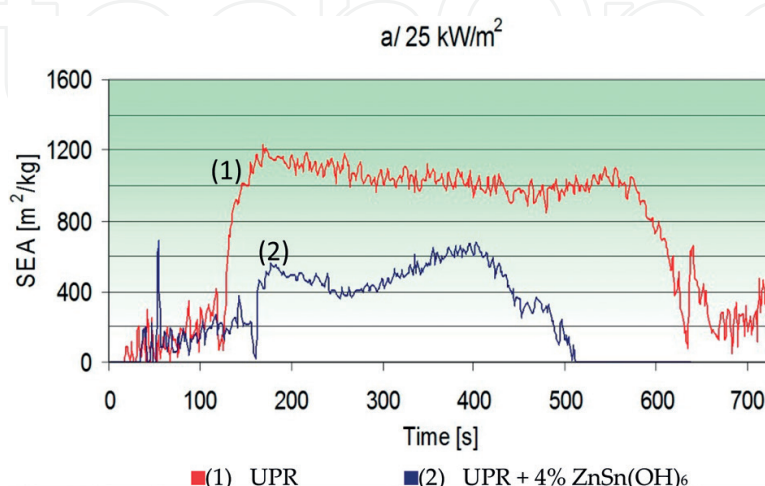


Figure 4. Smoke extinction area at radiation of 25 kW/m².

we also found the smoke suppressing and char incandescence reducing action after the extinction of the flame burning. We noticed that this modifier improved the “enclosure” of the surface of the sample burnt by the formation of a dense protective film.

3.2.3. Flame-retardant polyester resins by using hybrid modifiers

Initial assessment of an impact of a compilation of halogen-free flame retardants of flammability level of polyester compositions, performed as LOI evaluation, pointed to an especially favorable impact of melamine polyphosphate used in combination with expandable graphite/precipitated silica. A relatively small quantity of a combination of these flame retardants used in a proportion of 15 parts by weight to 5 parts by weight, respectively, led to an increase in LOI by 20–35% for samples of resins without and with reinforcement of a glass-reinforced polyester resin fiber compared to nonmodified resin only (**Table 1**) The polyester glass laminates GRP were obtained with the discussed composition as a matrix was characterized by LOI > 32–35%.

MMT modifiers showed a slightly worse flammability reduction impact, which was commented upon in the introductory part of the publication.

Thermogravimetric analysis of selected polyester compositions was performed in dynamic conditions at a heating rate of 20 K/min in air or nitric conditions — (**Figure 5**). Analysis of thermogravimetric curves (TGA) of the process of sample decomposition confirmed a different course of thermal decomposition of a nonmodified sample compared to compositions tested analogically and containing multi-ingredient flame retardants. The sample in which FR were made mass loss is much smaller at the same temperature as compared to reference sample. This is

Resins	Antipyrines	Oxygen index (LOI). %		
		PN-EN ISO 4589-2:1999/A1:2006		
	Conventional FR + Nanofillers	Content, weight %	Polyester composites	Polyester GRP laminates
Polimal 103A-UP ₁	-	-	19.7	-
DION 9500-UP ₂	-	-	21.2	22.8
UP ₁	MPP	15	2.5	33.1
UP ₁	MPP + oMMT	15 + 5	28.1	34.1
UP ₁	MPP+ EG	15 + 5	27.3	35.8
UP ₁	MPP + n SiO ₂	15 + 5	28.7	-
UP ₂	MPP	15	26.8	3.7
UP ₂	MPP + oMMT	15 + 5	27.7	3.3
UP ₂	APP + oMMT	15 + 5	27.2	-
UP ₂	MB + oMMT	15 + 5	27.5	-

Table 1. Determination of limited oxygen index according to PN-EN ISO 4589-2:1999/A1:2006.

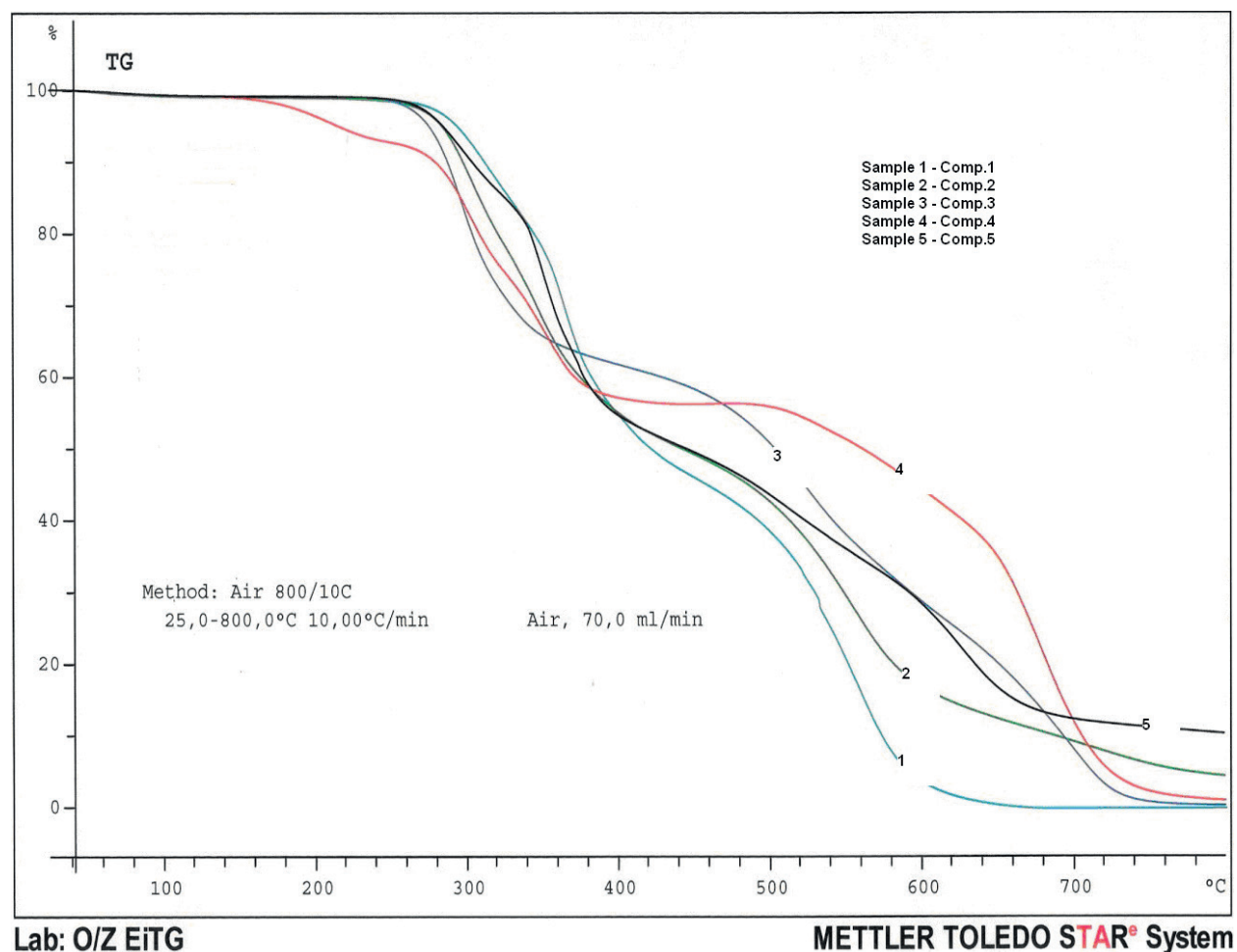


Figure 5. Thermogravimetric analysis of selected polyester compositions: 1-UP, 2-UP + 10MPP + 5oMMT, 3-UP + 10MPP + 5nSiO₂, 4-UP + 10MPP + 5EG, 5-UP + 15MPP + G. time, s,UP—unsaturated polyester resin, MPP—melamine polyphosphate, MMT—organophilic montmorillonite, nSiO₂—nanosilica, EG—expandable graphite.

the proof of the retardant action of these N/F with nanofiller system. As one can see, thermal decomposition of a non-modified polyester resin starts at around 300°C and proceeds in a single stage up to a temperature of around 430°C. *maximum* decomposition rate takes place at a temperature of around 350°C as determined on the basis of the DTG curve. Samples which contain a flame retardant, especially MPP and expandable graphite or precipitated nanosilica, undergo basic decomposition at around 420°C. Introduction to the system of multi-ingredient, especially selected flame retardants led to an increase in the quantity of solid decomposition leftovers.

The unmodified UP and the selected composites of UP with the PPM/nanomodified were investigated by means of TG analysis. For all samples, the process of thermal decomposition begins above 200°C, the differences in weight loss from samples appear and they become more distinct with an increasing temperature. The nonmodified UP loses 98% of its weight at 450st.C due to almost complete combustion process in nitrogen atmosphere. Referring to expectations, UP with FR modifiers (PPM 15 wt.% with EG 5 wt.%), has lower weight loss (85%) at the same temperature. This is partly due to high thermal stability of EG component, which loses only about 25% of its weight at 450st.C. For UP containing the compounding of PPM 15 wt.% and 5 wt.% oMMT, a slightly higher weight loss was observed. The same weight

loss at 450st.C was obtained for UP modified with the compounds of PPM/EG used in the amount of 25 weight parts per 100 parts of UP. All the modified UP with PPM/EG additives yields about 10 wt.% of char residue at 600st.C, which also may contribute to their FR action shown on the basis of flammability analysis.

The cone calorimeter (CC) measuring principle is that of oxygen consumption. This states that there is a constant relationship between the mass of oxygen consumed from the air and the amount of heat released during the polymer degradation.

The cone calorimeter test was followed up by HRR curves illustrating changes in heat release rate as a function of burning time. Heat release is shown as power per unit of exposed test surface. HRR curves for a polyester without and with fireproofing in the function of heat flux 50 kW/m² are shown in **Figure 6**. Analysis of HRR and MLR (**Figure 7**) curve shapes for compositions with flame retardants makes it possible to conclude that after the actual maximum increase in HRR, heat release rate decreases in a significantly shorter time compared to an analogically tested sample of a nonmodified polyester sample, and there is no second HRR peak. It should be contributed to an isolating effect of flame retardants, thanks to which heat release rate gets stable over time depending on radiation power at constant.

These results tend to demonstrate that the improvements in flame retardancy for nanocomposites do not occur in the process in the gas phase but rather by a change of the combustion act in the condensed phase (**Figure 8**).

Analysis of SEM micrograph presented in **Figure 9** makes it possible to conclude that a multi-ingredient flame retardant was distributed evenly over a polymer matrix, and additions grinding level is sufficient to have a homogenous system without a tendency to agglomerate.

In **Figure 9a**, showing this test, MPP in combination with MMT was used in order to additionally confirm homogenous morphology of compositions obtained this way.

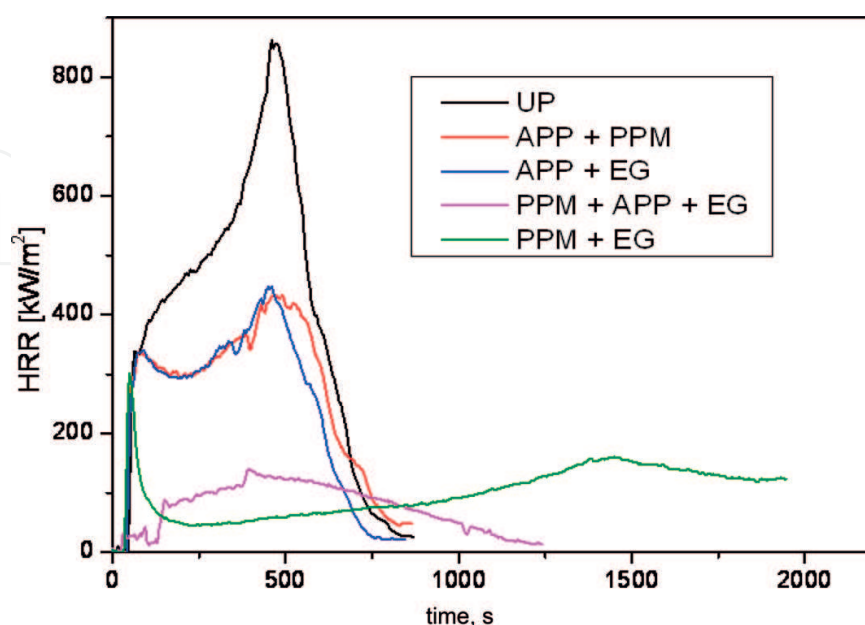


Figure 6. Course of heat release rate (HRR) versus combustion time (unsaturated polyester resins modified flame retardants).

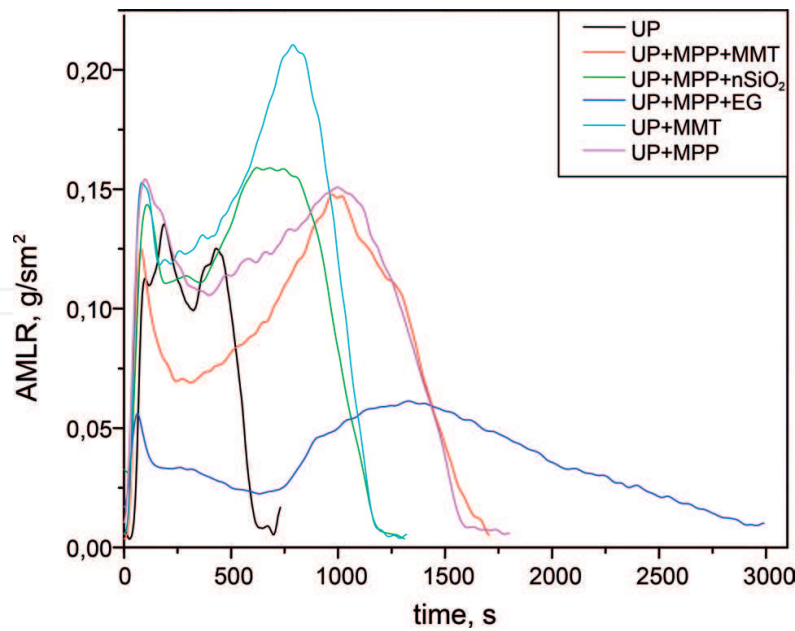


Figure 7. Course of mass loss rate (MLR) versus combustion time (UP resins).

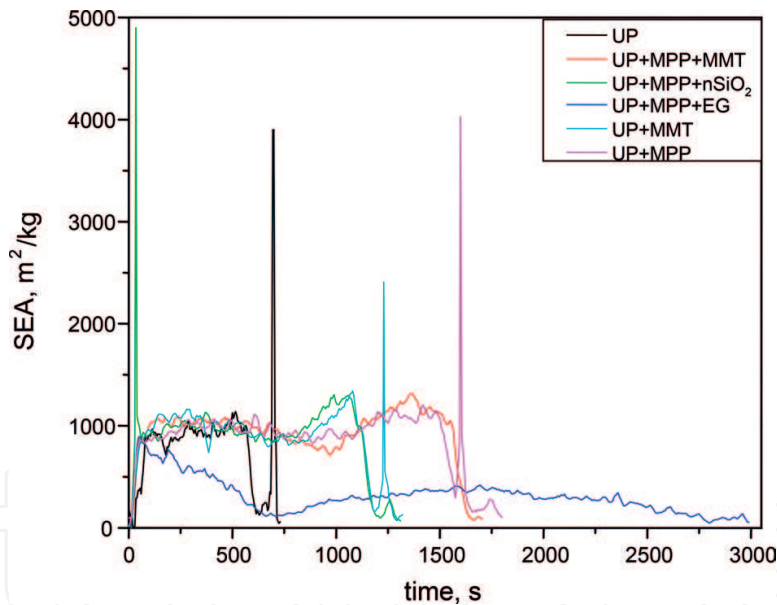


Figure 8. Course of specific extinction area (SEA) versus combustion time (UP resins).

SEM test performed for the surfaces of polyester compositions tested before and after burning by a cone calorimeter method confirmed intumescent impact of a phosphorous-nitrogen-based modifier, namely melamine polyphosphate MPP. In **Figure 9b**, showing this test, MPP in combination with EG was used in order to additionally confirm homogenous morphology of compositions obtained this way.

Synergy effect of expandable graphene, nanosilica and MMT with conventional flame retardants and their positive impact on thermal resistance and polymer burning profile were confirmed. Our tests suggested that there are at least two processes which reduce flammability

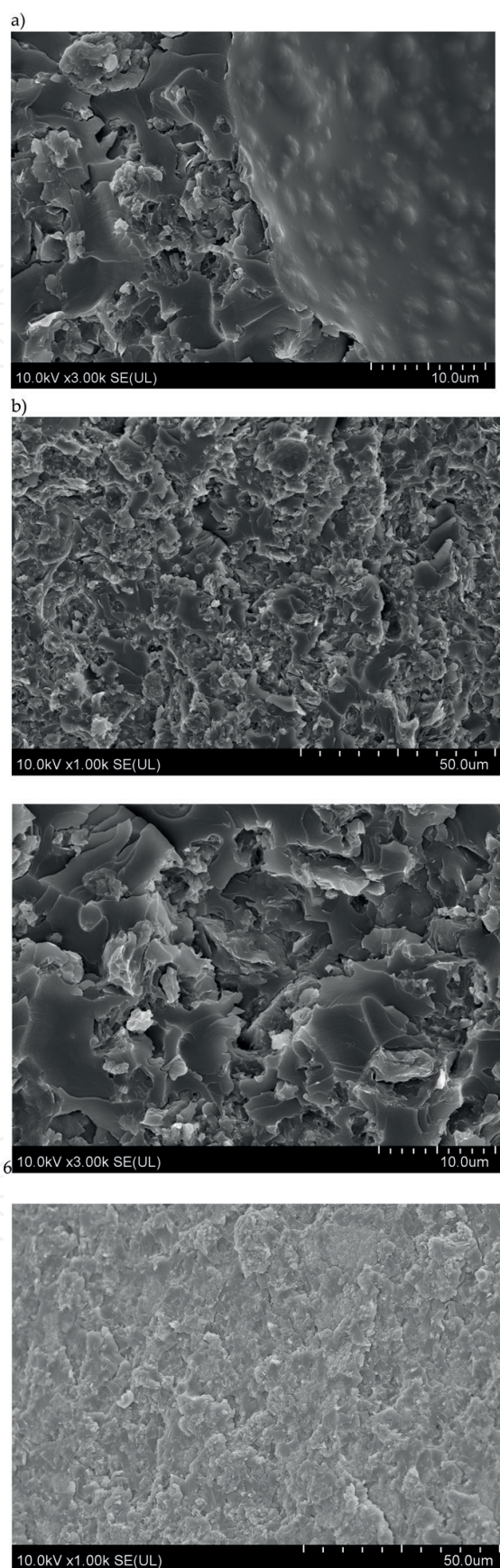


Figure 9. SEM micrographs (a,b) – Cross section of polyester resins modified with inorganic–organic fire retardants: a) SEM image of UP +15% MPP+ 5% o-MMT, b) SEM image of UP + 15% MPP + 5% EG.

level of polymers tested. In the first of them, a nanofiller had a positive impact on coke formation, and in the other one, non-flammable organic material influenced nanosilica /MMT dispersion, and in consequence, barrier properties reduce gas diffusion. Synergy effect was also observed while using traditional flame retardants and expandable graphite or while modifying selected melamine salts and this graphite structure which is active mainly in the solid phase, reducing toxic fume emissions in an effective way.

4. Conclusions

1. Halogen-free modifiers give possibility to obtain ecological polymer composition and a new class of flame-retardant thermoset polymer systems.
2. Commercially available flame retardants such as ATH or halogen-containing compounds are effective; however, the mechanical properties and processing of those polymers are often negatively influenced by the large quantities of halogen FR additive that are needed. The addition of those FR often increases the production of soot and carbon monoxide.
3. Nanocomposites have many advantages over the traditional flame retardants. Processing of nanocomposites is straightforward, and as the nanocomposites, no additional halogen is considered as an environmentally friendly alternative.
4. Nanocompounds are only a partial solution to a problem of reducing flammability of thermoset polymers. oMMT clay impact, mainly due to significant difficulties in its proper dispersion in a polymer matrix, is not fully convincing. Large specific surface of a nanofiller and a tendency to form a carbonized barrier layer should indeed promote thermal stability and reduction in a composite flammability level, but the catalytic effect of intercalation elements (flammable quaternary ammonium salts) in oMMT may lead to increased thermal degradation of thermoset polymers.
5. An effective solution was to use phosphorous-ammonium-based modifiers as conventional modifiers in a compilation with nanocompounds, mainly expandable graphite and precipitate nanosilica. Multi-ingredient flame and smoke inhibitors showed a positive impact on significant reduction in HRR by approx. 38–70% (determined by a CC test), increase in LOI by around 20–35%, and favorable profile of thermogravimetric curves (TGA) for modified polymers.
6. Micrograph images of nanocomposites performed by SEM confirmed good distribution of multi-ingredient systems in a duroplastic matrix without a tendency to agglomerate or sediment. Multi-stage technique of modifier intercalation with an ultrasonicator turned out to be an effective method of obtaining homogenous nanocomposites with the share of tested resins.
7. The concept of using multi-ingredient flame and smoke retardants made is possible to reduce the quantity of flame retardants used for obtaining the desired flammability level in products. This fact contributes to slightly negative influence of the modifications on

physical and chemical properties and strength parameters of polymers after setting. It is a significant step ahead for the techniques in the processing of thermoset polymers, and nanocomposites have many practical advantages over traditional flame retardants.

8. A multi-ingredient combination of flame retardants turned out to make significant progress in achieving a desired flammability level in thermoset resins. It should be assumed that the presence of conventional flame retardants led to a synergy effect promoting faster formation of a carburized protection layer hindering oxygen flow-through and emission of low-molecule compounds resulting from the process of polymer thermal destruction.

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