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FLAME RETARDANTS OF POLYMERIC MATERIALS

– CALCULATION OF THE OXYGEN INDEX

ANTYPIRENY MATERIAŁÓW POLIMEROWYCH

– OBLICZENIA INDEKSU TLENOWEGO

Abstract

This work presents problems associated with the flammability of polymeric materials which are widely used in many industries (PP, PE, PVC, PS, PET). The first part of the article discusses and characterises the methods of flame retarding polymeric materials, through their modification with a suitably selected fire retardant. The second part of the work presents the possibility of assessing the flammability of polymer materials, without performing laboratory tests, using the oxygen index method (*OI*). A two Johnson equations and the van Krevelen equation were used in the calculations. The strongest agreement between the results of *OI* and experimental values was obtained from the Johnson equation for PE and PP, and for PS from the van Krevelen equation.

Keywords: polymeric materials, flame retardants, oxygen index

Streszczenie

W pracy przedstawiono problematykę związaną z palnością materiałów polimerowych, powszechnie stosowanych w wielu gałęziach przemysłu (PP, PE, PVC, PS, PET). W pierwszej części artykułu omówiono i scharakteryzowano sposoby zmniejszania palności materiałów polimerowych, poprzez ich modyfikację odpowiednio dobranym antypirenem. W drugiej części przedstawiono możliwość oceny palności tworzyw polimerowych, bez wykonywania badań laboratoryjnych, za pomocą metody indeksu tlenowego (*OI*). W obliczeniach wykorzystano dwa równania Johnsona oraz równanie van Krevelena. Największą zgodność wyników *OI* z wartościami eksperymentalnymi otrzymano z równania Johnsona dla PE i PP, a dla PS z równania van Krevelena.

Słowa kluczowe: materiały polimerowe, antypireny, indeks tlenowy

1. Introduction

Polymeric materials have become valued on the market due to their physical and mechanical properties. The main reasons for the increase in the importance of plastics include their low price, resistance to corrosion and chemicals, mechanical strength, impact resistance, ease of forming, and the possibility of recycling way [1].

The possibility of using plastics in many branches of the economy has led to the development of new methods for the measurement of flame retardancy. One of the methods used to delay the combustion process is the use of combustion inhibitors. The correct choice of fire-resistance enhancing agent requires considerable knowledge of many fields related to the combustion process, examples include chemical kinetics, heat and mass transport theory, mechanics and fluid dynamics. The selection process is further complicated due to the existence of a large number of materials that differ in construction and composition. Due to the different properties and chemical compositions of different materials, a huge range of flame retardants has been created [2].

Currently, the production of polymers and flame retardants is one of the fastest growing branches of the chemical industry. At present, the global consumption of flame retardants exceeds two million tons per year. It is predicted that in 2018, the global consumption of flame retardants will total almost three million tons. About 85% of flame retardant manufacture is used for the production of plastics, the rest is used in rubber and textile products [3].

Figure 1 shows the actual and predicted applications of flame retardants over ten years from 2014. They are used in plastics, electrical devices, and wires and cables to treat potentially flammable materials. An increasing tendency of applications of flame retardants is observed, mainly due to the development of production of polymeric materials, but also introduced regulations and restrictions on fire protection and environmental protection.

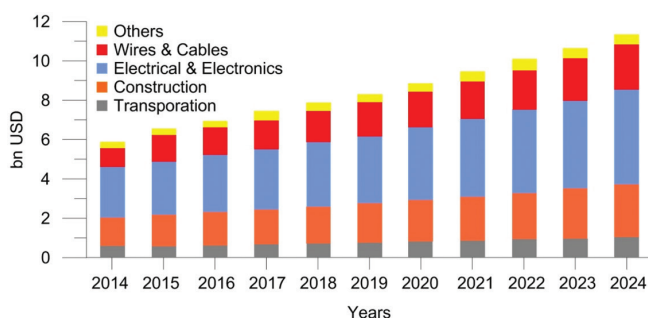


Fig. 1. The global flame retardants market 2014–2024 [4]

2. Flame retardants used for reducing the flammability of materials

Currently, the most frequently applied method of flame retarding polymers and polymeric materials is the use of flame retardants (FR). The growing demand for plastics in many industrial sectors has led to the development of fire retardant production.

Flame retardants are a diverse group of chemicals that are added to materials to reduce their flammability. The right choice of flame retardants is not easy due to the very large amount of different polymeric materials which differ with regard to their construction and composition. When selecting the quantity and type of flame retardant, it is also necessary to take into account the destination of the product, which we want to protect and the degree of fire hazard [5]. However, there are certain requirements that should be met by any well-chosen flame retardant [2]:

- a) chemical and physical stability during usage,
- b) no degradation of the physical and mechanical properties of the materials,
- c) the formation of a homogenous mixture with a polymer matrix,
- d) high level of effectiveness with low content in the material,
- e) the lowering of the temperature of pyrolysis and changing its course,
- f) the lowering of the temperature of the material and catalysing the heat-absorbing reaction,
- g) the emission of non-flammable gases that dilute the pyrolysis products and the inhibition of ignition,
- h) no emission of toxic substances that are conducive to corrosion processes,
- i) resistance to UV radiation and water,
- j) affordability and availability on the market,
- k) environmentally friendly.

The main purpose of using flame retardants is to interrupt the self-sustaining burning process of the material, which is shown in Fig. 2.

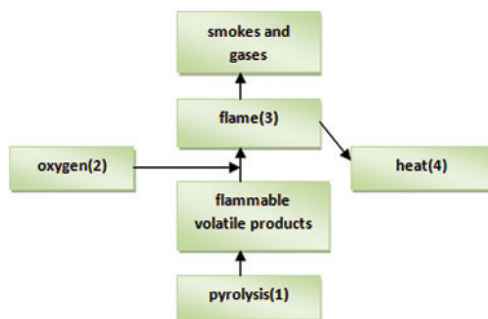


Fig. 2. Diagram of the self-sustaining process of burning material [6]

Stages 1 to 4 represent the points at which the combustion process can be interrupted by the use of flame retardants. Flame retardants can interfere with this process by [6]:

- 1) changing the course of pyrolysis by creating a charred protective barrier and reducing the amount of flammable, volatile, low molecular weight products;
- 2) cutting off the oxygen supply;
- 3) reducing the rate of flame propagation with compounds that deactivate free radicals, e.g. halogen compounds;
- 4) limiting the amount of heat released to prevent further pyrolysis.

2.1. The mechanism of flame retardant action

Due to the complexity of the combustion process, the mechanism of the action of flame retardants is difficult to determine. Its course is influenced by both chemical and physical reactions. From a chemical point of view, combustion is the reaction of the oxidation of organic compounds accompanied by heat emission. The combustion process starts with ignition, which initiates the energy stimulus. When the temperature is very high, there is also a risk of self-ignition. As the temperature rises, the individual combustion stages follow. The first stage is the elimination of functional groups, halogen atoms or water molecules. The second stage is the cracking of chemical bonds and the formation of small molecule compounds. The third stage is the oxidation of the resulting thermal decomposition products [7, 8]. The combustion process can occur according to several mechanisms simultaneously. The effects of the combustion process include the physical and chemical construction of the polymer and the flame retardant, ambient conditions and the presence of other modifiers [2].

2.1.1. The chemical mechanism of flame retardants

The chemical modification consists in the use of reactive flame retardants. These retardants form a coherent whole with the polymer via a covalent bond, making it difficult to isolate them from the polymer matrix. Their addition to the polymer means that they do not move to the surface of the material and do not oxidize during use. Chemical reactions affecting the combustion process may occur either in the gas phase or in a solid phase. The reactions in the gas phase lead to the deactivation of free radicals; this produces more favourable conditions for the occurrence of the combustion process. As a result of the polymer-flame retardant reaction, products are formed that scavenge the radicals from the surface of the polymer or react with them to deactivate them. Decreasing the activity of radicals reduces the flame temperature and the burning rate. There are two categories of solid phase reactions. The first of these concerns the creation of low molecular weight compounds with low melting points, which lower the temperature in the combustion zone and inhibit the propagation of flames. The second category is related to the formation of a porous carbon layer on the surface of the polymer. Reactive flame retardants include organic compounds containing non-flammable elements, for example: polyols, hexabromo phthalate. The reactive fire retardant can also be a functional group, a fragment of the molecule or an element that inhibits the combustion process [2, 8].

2.1.2. The physical mechanism of flame retardants

An alternative solution to reduce the flammability of materials is physical modification; this involves the use of additive (non-reactive) flame retardants. Unreactive fire retardants do not form an integral part of the material, they are introduced into finished products as part of the manufacturing process. They are usually used as mineral fillers, plasticisers, protective coatings, and compounds capable of decarboxylation and dehydration.

The physical mechanism of the action of flame retardants is based on [2]:

- a) reducing the degree of polymer degradation;
- b) the creation of insulating and barrier layers that block the flow of energy and mass between the solid and gaseous combustion phases;
- c) change of the thermal state of the polymeric material with the use of additives of high thermal conductivity and heat absorbing inhibitors;
- d) dilution of volatile pyrolysis products with non-flammable gases;
- e) extending the duration of pyrolysis.

2.2. Classification flame retardants

Flame retardants can be divided into two basic groups:

- a) Flame retardant compounds associated with the polymer during synthesis or crosslinking. These compounds are mainly used to reduce the flammability of epoxides, polyesters and polyurethanes. Examples of such compounds are polyols containing nitrogen, phosphorus and halogens.
- b) Non-reactive compounds relative to the polymer added at the time of processing, mainly used in the case of thermoplastics. This group includes halogen compounds, brominated diphenyl oxides, chlorinated and brominated paraffins, hydroxides, bromine and antimony compounds.

Table 1. Classification of flame retardants [2, 5, 9]

Group	Example	Properties
organic halogen compounds	decabromodiphenyl oxide (DECA)	strong resistance to high processing temperature and atmospheric ageing of products; does not affect the colour of materials; is added to the polymer in low concentrations
	dechlorane plus	has a high melting point which does not affect the degradation of the polymer or change its colour; increases the modulus of elasticity and thermal capacity of the polymer without diminishing the insulation properties and resistance to external factors
phosphorus compounds	red phosphorus	reduces smoke emission and corrosion in decomposition products; forms a thermal insulation layer on the surface of the burnt material
	phosphoric acid	is a volatile product of the destruction of phosphorus compounds; forms on the surface of the material; accelerates the carbonation process; eliminates volatile combustible products
	guanylurea phosphate	a compound used to impregnate and reduce the flammability of wood
inorganic hydroxides	aluminium hydroxide	has the form of white powder; forms on the polymer surface as a glass layer that inhibits the spread of flame; reduces the toxicity of fumes; reduces endothermic dehydration
	magnesium hydroxide	white, crystalline powder; shows greater thermal stability than ATH; reduces smoke emission; changes the colour of smoke from dark to light

Table 1 (cont.)

other inorganic compounds	basic aluminium oxalate (BAO)	white powder; reduces flammability and improves the electrical properties of materials
	aluminium salts of phosphoric acid	combustion inhibitors of oxygen-containing polymers in the main chain
	boron compounds	effectively operate in the condensed phase; capable of endothermic reactions leading to the release of water and the formation of a protective vitreous layer; enhance the action of mainly chlorine inhibitors; reduce smoke emission
tin-zinc compounds	zinc hydroxystannate (ZHS)	small size; very low toxicity; flame retardation and smoke formation; the ability to create a surface barrier; blocking the transport of heat from the combustion zone to the deeper layers of the material
	zinc stannate (ZS)	

3. Determination of the flammability of a selected group of polymeric materials

There are many methods for testing the flammability of polymers and polymeric materials. One of the most frequently applied is the oxygen index method. This is a very accurate method, which produces repeatable results for samples that burn completely, even if the tests are conducted in different laboratories. This method can also identify the flammability of materials that do not completely burn, but in this case, the measurement accuracy is lower. The existence of many theoretical correlations between the value of *OI* and other properties determining the flammability of materials makes it possible to determine the combustibility of the material without performing tests [2, 8].

3.1. Combustion reactions of selected polymeric materials

Three theoretical equations have been selected for calculation; these enable determining the value of the oxygen index by knowing other parameters related to the flammability of a given material.

- 1) Johnson's equation $OI = 7.95 \cdot 10^5 \cdot Q^{-1}$
- 2) Modified Johnson's equation $OI = 0.0184 \cdot M \cdot N_x^{-1}$
- 3) Krevelen's equation $OI = 17.5 + 0.4 \cdot CR$

where:

- OI* – oxygen index,
- Q* – heat of combustion,
- M* – molecular weight of monomer,
- N_x – the number of moles of oxygen,
- CR* – char residue.

Table 2 presents the combustion reactions of selected materials. The total combustion reaction is presented due to the fact that most of the selected materials are burned without

leaving a solid residue, which is characteristic of total combustion. In addition, the selected equations give more accurate results if the material burns completely.

Table 2. Combustion reactions of selected polymeric materials

Material	Chemical formula	Combustion reactions
polypropylene	C_3H_6	$C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O$
polyethylene	C_2H_4	$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
polyvinyl chloride	C_2H_3Cl	$C_2H_3Cl + 2.5O_2 \rightarrow 2CO_2 + H_2O + \uparrow HCl$
polystyrene	C_8H_8	$C_8H_8 + 10O_2 \rightarrow 8CO_2 + 4H_2O$
poly(ethylene terephthalate)	$C_{10}H_8O_4$	$C_{10}H_8Cl + 10O_2 \rightarrow 8CO_2 + 4H_2O$

The parameters necessary for calculations are presented in Table 3.

Table 3. Parameters used in calculations [2, 10]

Material	Heat of combustion [MJ/kg]	Molecular weight of mer [g/mol]	Number of moles of oxygen [mol]	Char residue [%]
polypropylene	44	42	4.5	0
polyethylene	44.5	28	3	0
polyvinyl chloride	20	62.5	2.5	15.3
polystyrene	40.5	104	10	0
poly(ethylene terephthalate)	22	192	10	5.1

3.2. Calculated *OI* values for materials based on empirical equations

The table and figure below present the calculation results calculated from individual equations. For each material, the calculated value of the oxygen index was compared to the experimental value with and without the addition of flame retardant.

The materials were classified according to the flammability criterion characteristic of the oxygen index method [2] :

- ▶ $OI \leq 21\%$ – flammable,
- ▶ $OI > 21\%$ – retardant,
- ▶ $OI > 60\%$ – non-flammable.

The calculations show that for compounds which burn completely without leaving any solid residue, the equations above are better suited than materials that do not completely burn. These compounds are polypropylene, polyethylene and polystyrene. In the case of these materials, slight differences between the value of the oxygen index determined experimentally

and calculated from theoretical equations can be observed; the errors are on average: 0.47% (PP), 0.49% (PE), 1.26% (PS). Johnson's equation works best for polyethylene and polypropylene with regard to the heat of combustion. In the case of polystyrene, the highest consistency of results is obtained using van Krevelen's equation, which takes into account the amount of solid residue after combustion.

Table 4. Calculated *OI* values for materials based on empirical equations [2, 8, 11, 12]

Material	Experimental <i>OI</i>		Theoretical <i>OI</i>			Classification
	without FR	with FR	Johnson's equation	Modified Johnson's equation	Krevelen's equation	
PP	0.185	0.240	0.181	0.172	0.175	flammable
PE	0.180	0.230	0.179	0.172	0.175	flammable
PVC	0.220	0.280	0.398	0.460	0.236	flammable
PS	0.175	0.240	0.196	0.191	0.175	flammable
PET	0.210	0.235	0.361	0.353	0.195	flammable

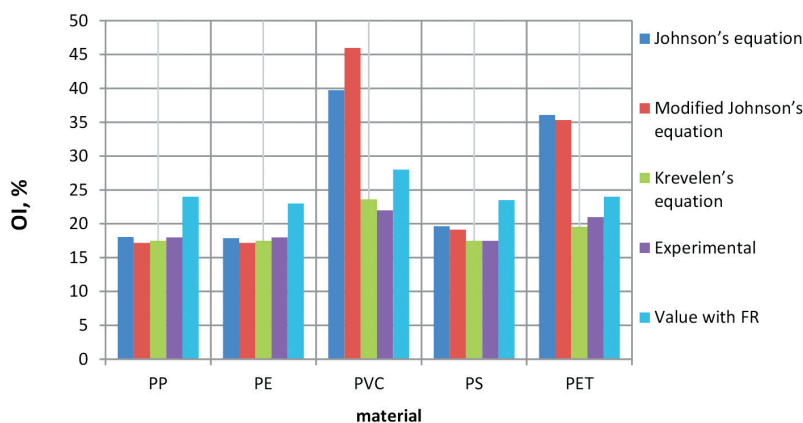


Fig. 3. Oxygen index values for a selected group of polymeric materials

Compounds that are not completely burned, give worse results in the applied theoretical equations. Only in the case of poly (ethylene terephthalate) and polyvinylchloride, does no combustion occur. These polymers leave a char residue. The resulting coke layer protects the material, limiting the access of oxygen and thus inhibits the progress of destruction. This involves more O_2 being needed to initiate the combustion reaction.

Upon analysing these materials, larger discrepancies were found between the theoretical value and the laboratory value. The average error value for PVC is 14.5%, and for PET it is 10.3%. Both polyvinyl chloride and poly (ethylene terephthalate) used in solve the Johnson equation, give to the worst results. The explanation for this may be the low value of the heat

of combustion. It can be observed that the value of the heat of combustion in their case is twice as low compared to the heating value of PP, PE and PS. An additional effect on the deterioration of the applicability of these equations is the presence of the chlorine atom in the PVC molecule. Johnson equations, taking into account both the heat of combustion and the molecular weight of the mer and the moles of oxygen, provide exact results only if the material contains carbon, hydrogen and oxygen in its composition.

4. Summary

- ▶ The possibility of using polymeric materials in many industrial sectors has influenced the development of new methods for reducing and testing flammability.
- ▶ The reason for the increase in the production of flame retardants is not only the ever-growing demand for polymeric materials but also the regulations and restrictions on fire protection and environmental protection.
- ▶ Until present, no flame retardant has been found that meets all the characteristics of a good combustion inhibitor.
- ▶ The applied Johnson and Krevelen models only partly take into account the structure of the material, the composition and shape of the polymer as well as the conditions of combustion of the sample. The value of the oxygen index determined theoretically should be treated as an approximate value.
- ▶ By comparing the value of the oxygen index for individual materials both with and without the addition of FR, one can assess the effectiveness of their operation. It is observed that after the addition of flame retardants, there is an increase in the *OI* value and thus, the flammable properties of the analysed materials are improved. The size of the growth of the *OI* value is undoubtedly influenced by the type of flame retardant used and also by the type of material.
- ▶ Compounds that burn completely meet the requirements of the Johnson (PE, PP) and the Krevelen (PS) equations ($\delta OI \sim 0.7\%$). The calculated oxygen index for PVC and PET materials after combustion (which leaves coke breeze) significantly differs from the experimental value ($\delta OI \sim 12.4\%$).
- ▶ The increase in the *OI* value is influenced by the type of flame retardant used and type of material.

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