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THE EFEKT FIRE FIGHTING FOAMS ON THE ENVIRONMENT AND FIRE EXTINGUISHING

Abstract

Extinguishing foams are commonly used for extinguishing the fire of flammable liquids, whereby their insulating, choking and quenching effects are exploited. The purpose of this paper is to consider and compare foams currently used in Slovak fire departments, with respect mainly to their high extinguishing effect (capability of faster aborted burning on a large surface at low foam consumption), but also their impact on the environment in each stage of their life cycle. Fire fighting foams are commonly used to reduce the spreading and extinguishing of Class B fires and to prevent re-ignition. These foams can be used to prevent ignition of flammable liquids and in certain conditions for extinguishing Class A fires. Foams can be used in combination with other extinctive substances, mainly gaseous and powders ones. Modern fire-fighting foams can be considered to be very good in terms of physical characteristics, but in recent years, the REACH legislation draws attention to their ecotoxicological properties. If fire-fighting foams are used to extinguish large fires, their products (such as decomposed water from the formed foam) are very likely to get into the soil and water flow, concurrently affecting the possibility of wastewater purification. All types of foam have different ecological characteristics since their components determine the rate of biodegradation. The ecotoxicological tests of *Sinapis alba* also showed that even a low concentration of foamer exhibits significant toxicity. This paper describes an analysis for four foams: Sthamex AFFF 1 %, Sthamex AFFF F-15, Pyronil, Moussol APS F-15. It is necessary to know their physical characteristics, e.g. their stability at low and high temperatures defined by half-life; the number of foamings specifying whether it is heavy, medium or light foam, and also their viscosity properties to be appropriately selected and used in fire-fighting practice.

Streszczenie

Piany gaśnicze są zazwyczaj używane do działań gaśniczych pożarów cieczy palnych, przy których wykorzystane są ich właściwości izolacyjne, uszczelniające oraz tłumiące proces spalania. Celem tego artykułu jest podjęcie rozważań i analiza porównawcza powszechnie używanych pian gaśniczych w słowackim departamencie przeciwpożarowym, rozpatrując nie tylko ich wysoką skutecznością gaśniczą (zdolność podawania ich podczas gaszenia pożarów o dużej powierzchni, przy niskim poziomie ich zużycia) ale również ich oddziaływanie na środowisko naturalne uwzględniając ich każdy cykl życia. Piany gaśnicze są zazwyczaj używane w celu zmniejszenia rozprzestrzeniania strefy spalania i gaszenia pożarów klasy B oraz zapobieganiu ponownego ich zapalenia. Piany użyte w analizie są używane do ochrony przed zapłonem rozlewisk cieczy palnych i w pewnych warunkach do gaszenia pożarów klasy A. Piany testowane mogą być użyte w kombinacjach z innymi substancjami tłumiącymi proces spalania, głównie gazami i proszkami. Współczesne piany gaśnicze muszą posiadać nie tylko odpowiednie właściwości fizyczne ale również w ostatnich czasach muszą spełniać przepisy REACH dotyczące właściwości ekologicznotoksykologiczne. Jeśli piany gaśnicze używane są do gaszenia pożarów o dużych powierzchniach, to pod wpływem czasu, wyciekająca z piany woda, przypomina potok wody i gleby, który zmywa powierzchnię ziemi jednocześnie ją zanieczyszczając. Zastosowane w artykule wszystkie typy pian posiadają różne charakterystyki toksykologiczne, stąd też składniki pian decydują o szybkości biodegradowalności pian. Test toksykologiczny *Sinapis alba* ukazuje znaczącą toksyczność pian nawet przy ich niskich stężeniach. Artykuł ukazuje analizę dla czterech pian utworzonych ze środków pianotwórczych: Sthamex AFFF 1 %, Sthamex AFFF F-15, Pyronil, Moussol APS F-15. Jest niezbędna znajomość ich właściwości m.in. ich stabilności w niskich i wysokich temperaturach określonych jako czasy pół trwania, liczbę spienienia określoną dla ciężkiej, średniej i lekkiej piany a także ich lepkości w celu odpowiedniego wyboru rodzaju pian do prowadzenia działań ratowniczo – gaśniczych.

Key words: foams, fire extinguisher, fire, extinguishing properties, biodegradability of foamers;

Słowa kluczowe: piany, środek gaśniczy, właściwości gaśnicze, biodegradowalność środków pianotwórczych;

Introduction

Extinguishing agents are various substances and materials used to stop (slow down) the combustion process. Basic requirements for extinguishing agents are as follows:

- they must have high fire effects (the ability to quickly stop the burning of large areas at low consumption),
- they must not be harmful to human (living) organisms, when used or stored,
- they must be available at a reasonable price, etc.,

Fire-fighting foams play a significant role as extinguishing agents.

Characteristics of fire-fighting foams

Fire-fighting foam is an extinguishing agent composed of numerous bubbles formed mechanically or chemically from liquid. Chemical foam is formed by the reaction of alkaline solution with acidic solution in the presence of a foam stabilizer. Mechanical foam is formed after introducing air and/or inert gas into a foaming solution [1].

Foams belong to two-phase disperse systems consisting of dispersive media (liquid) with a dispersed phase - three-dimensional lamellae of permanent structure containing enclosed gas. Plate thickness ranges from 0.001 to 0.01 mm [2].

Foam fire effects consist of the following physical principles (Figure 1):

- Isolation - separate flammable substance from flame,
- Choky - prevents access of air oxygen to the flammable substance, prevents the evaporation of flammable liquids,
- Refrigerating - reduces the temperature of the burning substance and consequently slows down burning, which is directly proportional to the water content of the foam [3-9].

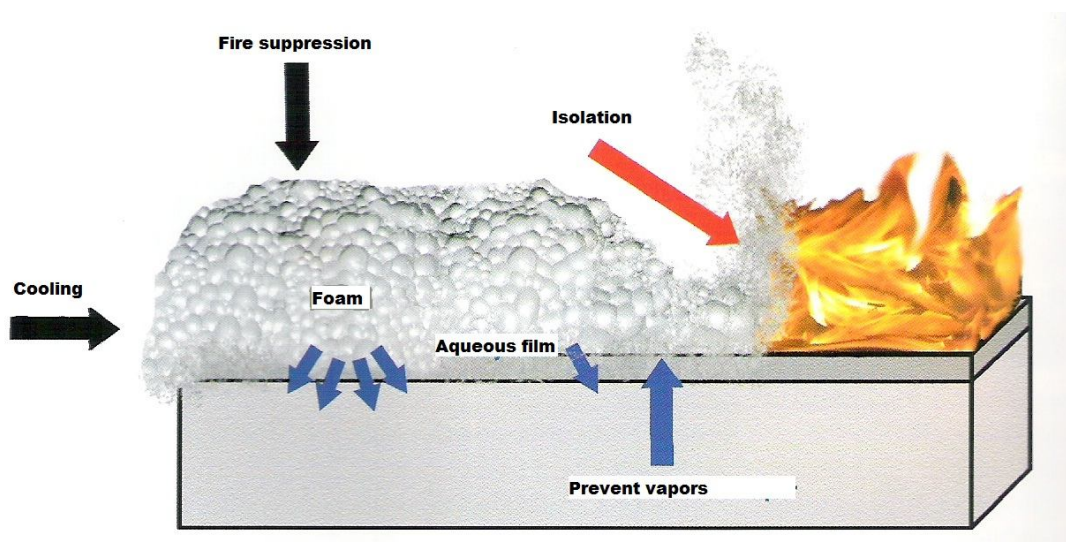


Fig. 1 Scheme of the mechanism of extinguishing using foam [3]

Rys. 1. Schemat mechanizmu gaśniczego podczas stosowania pian [3]

Fire fighting foams are commonly used to reduce the spreading and extinguishing of Class B fires and to prevent re-ignition. These foams can be used to prevent ignition of flammable liquids and in certain conditions for extinguishing Class A fires. Foams can be used in combination with other extinctive substances, mainly gaseous and powders ones [4]. The first foam fire extinguishers worked on a principle of chemical foam. Currently, works are underway on an air-mechanical foam or a foam that is formed at the moment of contact of a given foaming agents fire with fire [3].

Air-mechanical foam is prepared at the time of intervention of a mechanical mixture in a solution consisting of water and a foaming solution with atmospheric air in a foaming nozzle. The foaming solution rises in the mixer when injector sucks the foamer into the water. Foamer concentration in water usually ranges from 1 % to 6 %. Gas component can also be carbon dioxide, nitrogen or another inert gas [2].

Physical properties of foamers

A foamer is a liquid mixed with water at prescribed concentration to form a foaming solution. Foam is a dispersion system in which gas (air) is the dispersing agent and liquid is the dispersive environment (heterogeneous mixture of gas and liquids). It is an unstable system subject to rapid changes. The foam is a cluster of air bubbles generated from a foaming solution. The speed of this transformation is important to allow assessment of the stability of the foam [1]. Stability properties, as well as the effectiveness of foam and foamers, are determined by their physical and chemical properties. The monitored physical and chemical properties foamers and foams include:

- **Number of foaming** - ratio of the volume of produced foam to the volume of liquid, by which this foam was produced. This number indicates how many times the volume of foam exceeds the volume of foaming solution. Based on this number foams are divided into three groups (severe, moderate and light foam);
- **Viscosity** – this is an expression of fluidity of liquid, and depends on temperature (decreases with increasing, temperature);
- **Foamer frost resistance** - temperature at which the substance is liquid and does not begin to exclude solid parts;
- **Content of the sediment** - proportion of solid components in concentrates of foamers expressed in % vol.;

- **Foam stability** – it is influenced by excretion of water from the foam, defined by half-life, respectively quarter-life, which is the time required to eliminate half, respectively a fourth of water contained in the foam [1];
- **Half-life time of foam** - the time at which the foam releases 50% of foaming solution, given in minutes. The conversion speed is an important determinant of quality and stability of foam;
- **pH** - liquid reaction, i.e. acidity, alkalinity or neutrality expressed as the negative decimal logarithm of hydrogen ion activity;
- **Foaming solution spreading factor** - a measure that indicates the ability of one liquid to unfold spontaneously on the surface of another liquid; it is not an indicator of its quality; it is given in $\text{nM}\cdot\text{m}^{-1}$ [3].

The stability of foams depends on the structure of surface films from the so-called foaming agents, such as electrolytes, soaps, saponins, proteins, etc. In the process of fire-fighting, the foams are constantly disrupted by the influence of ignition heat, internal foam force and hot surface of burning liquid. It has been proven that the degradation rate of foam by flame heat effect is much smaller than on the actual surface of the heated evaporating liquid. In this process foams have an insulating and cooling effect. These effects depend on the type and quality of used foamers. More factors influence the quality; from a practical point of view, conditions and storage period of foams are of importance [6, 7].

Foam as the extinguishing substance is prepared at the time of intervention. The properties of foam and its quality are affected by the properties and purity of used chemicals, i.e. water, foaming agents and gas component (usually air). Used foaming equipment also has a substantial impact on the quality of foam.

The nature and application of particular foaming agents, it is possible to prepare foam at the moment of an instant action, regarding to particular fire. As for composition and the resulting properties, foamings are divided into the following groups [5]:

- Protein foamers (P),
- Fluorine-protein foamers (FP),
- Synthetic foamers (S),
- Alcohol resistant foamers (AR),

- Aqueous film forming foamers (AFFF),
- Fluorine-protein foamers forming a water film (FFFP) [4, 6].

Extinguishing properties of foamers are summarised in Table 1.

Table 1

Standard fire-fighting capabilities of different types of foamers [4]

Tabela 1.

Standardowe możliwości gaśnicze różnych typów środków pianotwórczych [4]

Type of foamer	Extinguishing Class ability*	Level of resistance to Reburn**	Film-forming
AFFF (no AR)	I	C	+
AFFF (AR)	I	B	+
FFFP (no AR)	I	B	+
FFFP (AR)	I	A	+
FP (no AR)	II	A	-
FP (AR)	II	A	-
P (no AR)	III	B	-
P (AR)	III	B	-
S (no AR)	III	C	-
S (AR)	III	C	-

* - results of PN EN 1568-3:2003 Fire Extinguishing Media - Foam Concentrates - Part 3: Specification for Low Expansion Foam Concentrates for Surface Application To Water-immiscible Liquids

** - results of PN EN 1568-3:2003, distribution into foamer resistance classes A, B, C and D, depending on when they are ignited vapor above the liquid covering the liquid with a small flame

Storage of foamers

One of the major factors that affect the properties of foamers and foams is their storage life. If foamers are stored in their original packaging according to the manufacturer's instructions, they may be used for several years without any change to their original characteristics. However, if a mixture of foamer and water (foaming solution) is ready for frothing and is located in the piping system or in vehicle tank, it must be changed each year.

Synthetic foamers must be stored in containers made of stainless steel or plastic. Protein foamers are stored in steel and metal containers. Zinc, tin or aluminium containers are not suitable for storage, as foamers are very aggressive in relation to such materials.

Valves, pumps and tanks for storage of foamers must be made of the same type of metal. If they came into contact with different types of metals, foamers would cause electrochemical corrosion. Foamers are very sensitive to temperature changes. Optimal temperatures are in the range from +5 to +25 ° C. No adverse effects on foamers' properties

were observed even within the temperature range of -15 to + 40° C. After re-thawing, foamers can be re-used since there are no changes to their basic physical and chemical properties or reduction in their fire-fighting effectiveness [3].

Foamers' impact on the environment

The combustion products and the combustion residues are much more harmful than the extinguisher used. Quickly extinguished fire often outweighs the negative impacts of the extinguishing agent by reducing the formation of toxic products and residues after burning. When extinguishing fires for example with water, which is considered to be harmless to environment, the effluent water contaminated by decomposed products of combustion may significantly pollute the environment over a long time horizon. Fires can be extinguished much faster by applying the fire fighting foams, which are environmentally acceptable by posing a smaller pollution risk to the environment.

Environmentally acceptable fire-fighting foams should have at least the same fire fighting capability as traditional foams made of protein or AFFF foamers with minimal environmental impact (water, soil). Traditional ingredients in foamers (tensides, ethylene glycol, butyldiglycol, propylene glycol, alkylpolyglycozide, nonylalcohol) are known to cause problems in terms of toxicity of the substances as such, with respect to their degradation products. Fish and aquatic organisms are highly endangered by the application of fire-fighting foams. However, when compared with chemical substances and preparations, the toxicity of foamers is low, yet some problems arise due to the secondary toxicity resulting from the long biodegradability of decomposition products in the environment.

Biodegradability of foamers means their ability to degrade in a biological or chemical way the original substance to environmentally acceptable decomposition products, for example by assimilation (water and carbon dioxide). Biological degradation is caused by microorganisms and fungi. Foamer degree of degradation is often given as the ratio of biochemical oxygen demand (BOD) and chemical oxygen demand (COD).

Biochemical oxygen demand is the amount of dissolved oxygen consumed by microorganisms over time, e.g. 5 days (BOD₅) in the biochemical decomposition processes of organic substances in water under aerobic conditions. This oxygen quantity is proportional to the quantity of present degradable organic substances, and it can be therefore estimated from

the BOD level of water pollution by extinguishing foam. Biochemical oxygen demand is determined in the original or a suitably diluted solution of foamer.

Chemical oxygen demand represents the amount of oxygen required for oxidation of organic substances in water using strong oxidants over time (usually two hours). It is the rate of total organic substances in water, and thus an indicator of organic pollution of water.

Biodegradability of foamer is expressed as a ratio of COD and BOD5 in percentage (%) biodegradation:

$$Bg = \text{BOD5} / \text{COD}$$

Bg - biodegradability

The perfect foam should have a full-degradability, and must not overly consume dissolved oxygen in water. Environmentally friendly foam (i.e. Green foams) should extinguish fires as effectively as traditionally used foams, but we have to know their degradation, otherwise there is no significance. They are several times more expensive than conventional foam, but on the other hand, their extinguishing capacity may several times exceed that of the fluorine-protein and AFFF foams (good quenching of the flames in AFFF and prevent re-overing typical for fluorine-protein foams).

Experimental

The aim of the experiment was to assess the extinguishing properties of foamers in the laboratory, and subsequently verify their impact on the environment in an experimental way.

The following measurements were therefore made:

- monitoring the numbers of frothing and foaming time,
- determining the half-life time,
- determining viscosity,
- determining the biochemical and chemical oxygen consumption,
- carrying out ecotoxicological tests on higher plants.

The following foamers were used in the experiment (Table. 2):

Table 2

Used foamers and their characteristics

Tabela 2

Nazwy i charakterystyki zastosowanych środków pianotwórczych

Name of foamer	Producer	Use for Classes of fires	Recommended concentration	Notes
Sthamex AFFF 1 %	Dr. Sthamer	A a B	1 %.	pecially designed for hydrocarbon fires, plastics and mineral oil products
Sthamex AFFF F-15	Dr. Sthamer	A a B	3 %.	Specially designed for fires of oil products and plastics
Pyronil	Chemtura Corporation	A a B	3 %	Synthetic multipurpose foamer, also light foam
Moussol APS F-15	Dr. Sthamer	A a B	3 %	Fire fighting of liquid of non-polar hydrocarbons
			6 %	Fire fighting of liquid of polar hydrocarbons

Their selection was based on the research findings available in Fire and rescue corps in Slovakia. Foamers were prepared in five different concentrations (1 %, 3 %, 6 % according to the manufacturer's recommendations and 9 % and 12 % only for comparison higher concentrations).

I. Assessment of foamers in terms of extinctive and physical properties

Number of foaming

The number of foaming (E) was determined in accordance with STN EN 1568-3: 2002 standard Technical conditions of foamers for heavy foam on the surface use with the liquid immiscible with water. The determination comprised the number of frothing of selected foamers of different concentrations, and the time of foam formation (Table 3).

Table 3

Number of frothing and time of foaming tested foamers

Tabela 3.

Liczba spienienia i czas spienienia analizowanych środków pianotwórczych

No	Concentration of foamer [%]	Number of frothing E				Time of foaming [s]			
		Sthamex AFFF 1 %	Sthamex AFFF F-15	Pyronil	Moussol APS F-15	Sthamex AFFF 1 %	Sthamex AFFF F-15	Pyronil	Moussol APS F-15
1.	12	4.886	4.909	4.901	4.822	6.61	16.58	17.71	19.23
2.	9	4.894	4.891	4.908	4.854	11.69	19.20	20.34	23.38
3.	6	4.890	4.827	4.878	4.887	13.35	19.25	25.63	26.20
4.	3	4.906	4.826	4.839	4.837	14.70	25.28	30.55	30.24
5.	1	4.827	4.883	4.820	4.807	27.35	35.04	34.44	57.81

Number of frothing ranged around the value 4.9 ± 0.1 for all foamers, allowing a fair comparison of foaming time. The fastest foamed foamers Sthamex AFFF 1%, AFFF Sthamex F-15, then Pyronil and the longest foaming time had Moussol APS F-15, in which time foaming at 1% concentration significantly extended.

Half-life time

As regards the manufacturer recommendations in the safety data sheets, half-life was tested by using 3% solutions, while monitoring the time at which 50% of the foaming solution were released from the foam. The results of the measured values for each foamer are given in Table 4.

Table 4

Half-life of tested foamers (3 % solutions)

Tabela 4.

Czas półtrwania pian

No	Name of foamer	Half-life time [s]
1.	Sthamex AFFF 1 %	62
2.	Sthamex AFFF F-15	166
3.	Pyronil	187
4.	Moussol APS F-15	187

The most favorable results were achieved with the use of foamers Pyronil and Moussol APS F-15 foamers, where the half-life was 187 seconds.

Measurement of foamer viscosity

Viscosity was determined according to DIN 53015:2001 Viscometry - Measurement of viscosity using the Hoesppler falling-ball viscometer for viscosity, etri Höppler KF 3.2, which is designed primarily to measure the dynamic viscosity of Newton's liquids. It measured the time of ball fall between two lines and the calculation of the viscosity was calculated from the relation:

$$\eta = t \cdot (\rho_1 - \rho_2) \cdot K, \quad (2)$$

where

η the dynamic viscosity in mPa.s,
 t falling time of balls in s,
 ρ_1 ball density in g.cm⁻³,
 ρ_2 density of the fluid in the bath temperature g.cm⁻³,
 K the constant mPa.cm³.g⁻¹.

The results are shown in Table 5.

Table 5

Measurement results of foamer viscosity

Tabela 5.

Lepkość analizowanych środków pianotwórczych

No	Name of foamer	t [s]	ρ_1 [g.cm ⁻³]	ρ_2 [g.cm ⁻³]	K [mPa.cm ³ .g ⁻¹]	η [mPa.s]
1.	Sthamex AFFF 1 %	124	2.224	1.07	0.07293	10.436
2.	Sthamex AFFF F-15	70	2.224	1.04	0.07293	6.044
3.	Pyronil	76	2.224	1.545	0.07293	3.466
4.	Moussol APS F-15	69	8.142	1.170	0.1225	58.931

The lowest viscosity was measured in foamers Pyronil a Sthamex AFFF F-15 foamers, the highest in Moussol APS F-15.

II. Foamer impact on the environment

Determination of biochemical oxygen demand

The basic part of the test is treatment and dilution of water sample to be analyzed by different amounts of diluent water with a high amount of dissolved oxygen and vaccinic aerobic microorganisms with prevention of nitrification. Incubation was conducted at 20 C within a defined time of 5 days in the dark in a full closed flask. The dissolved oxygen concentration was determined before and after incubation according to STN EN 1899-1 Water

quality - Determination of biochemical oxygen consumption after n days (BSKn): Part 1: Dilution and inoculation method with the addition of allylurea. Use was made of vaccinated diluting water, and dissolved oxygen was electrochemically determined (Table 6).

Determination of chemical oxygen demand

The oxidizable substances in the test sample volume are oxidized by a known quantity of potassium dichromate in the presence of mercuric sulfate and silver catalyst in an environment of concentrated sulfuric acid in a defined time interval. The COD value was calculated on the basis of the amount of reduced dichromate.

The indicator COD shows the total content of organic substances in water - organic water pollution (Table. 6).

Table 6
Results of COD and BOD5 values tested foamers (3% foreign solutions)

Tabela 6.
Otrzymane wartości COD i BOD5 dla badanych środków pianotwórczych (3% roztwory)

No	Name of foamer	COD [mg.l ⁻¹]	BOD5 [mg.l ⁻¹]	BOD5/COD [%]
1.	Sthamex AFFF 1 %	76.23	22 790	0.33
2.	Sthamex AFFF F-15	73.68	21 370	0.34
3.	Pyronil	79.20	33 530	0.23
4.	Moussol APS F-15	83.46	17 470	0.47

The results of foamer biodegradability suggest that foamers have little ability to biological degradation due to a very small proportion of degradable substances.

Acute toxicity

The acute toxicity is the ability or property of foamer to cause severe biological harm or death of an organism over a relatively short exposure time (24 - 96 hours). IC₅₀ was defined as inhibitory concentration of tested substance that causes a 50% inhibition of root growth of *Sinapis alba* plants (pure variety of white mustard, seed germination > 90 %, seed size 1.5 mm - 2.5 mm) for 72 hours.

The basic monitored parameter for the test evaluation is the average length of the roots. The value determined in the test solution was compared with the control one, and the percentage of inhibition (reduction) or stimulation (extension of the root) was calculated. Results are listed in the table 7.

Table 7

Results of ecotoxicological test for seeds of higher plants

Tabela 7.

Wyniki testów toksykologicznych przeprowadzonych na ziarnach wysokich roślin

No	Name of foamer	IC _{0,5} * %	IC ₁ %	IC ₂ %	IC ₃ %	IC ₅ %
1.	Sthamex AFFF 1 %	96.2				
2.	Sthamex AFFF F-15	87.6	88.3			
3.	Pyronil	98.0				
4.	Moussol APS F-15	66.2	76.7	87.9	89.6	98.3

* Ecotoxicological test on seeds of higher plants *Sinapis alba*, subscript reflects the concentration of sample (volume %). Empty box = no sprouted seed.

Ecotoxicological test shows that the higher concentrations are significantly toxic to the tested plant species.

Conclusion

Currently many types of fire-fighting foams different physical and extinguishing properties are known. Each of them has its own pros and cons, as was shown by our testing. It is necessary to know their physical characteristics, e.g. their stability at low and high temperatures defined by half-life; the number of foaming specifying whether it is heavy, medium or light foam, and also their viscosity and other properties to be appropriately selected and used in fire-fighting practice.

Modern fire-fighting foams can be considered to be very good in terms of physical characteristics, but in recent years, the REACH legislation draws attention to their ecotoxicological properties. If fire-fighting foams are used to extinguish large fires, their products (such as decomposed water from the formed foam) are very likely to get into the soil and water flow, concurrently affecting the possibility of wastewater purification. All types of foam have different ecological characteristics since their components determine the rate of biodegradation. The ecotoxicological tests of *Sinapis alba* also showed that even a foamer of low concentration exhibits significant toxicity.

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Specjalność – procesy spalania materiałów polimerowych
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