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SIMPLE FIRE MODEL FOR COMPARATIVE STUDIES OF CRITICAL CONDITIONS DURING COMBUSTION OF CHOSEN POLYMER MATERIALS

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Abstract. The time taken to evacuate space inside a building (required time for evacuation) must be shorter than the time for the environment in that space to become life threatening (available safe egress time – ASET). That time is the time, when certain tenability limits of smoke filling, toxicity and thermal influence of the building environment are exceeded. As a consequence of lost visibility in smoke, people loose their orientation, and consequently evacuation is slowed down or becomes impossible. In such conditions inhaling of an excessive volume of toxins may lead to loss of consciousness or death. In the paper are discussed the influences of visibility through a smoke layer (or smoke obscuration) and concentration of toxic products of combustion on ASET, in well ventilated fires. Apart from the visibility range, also CO and CO_2 concentrations have been chosen for the analysis. The given simple formulas show the dependency of rate of combustion and yields of smoke and toxic species on visibility reduction rate and increasing of concentration of toxic products evolved during combustion of selected materials. Epoxy materials were used for the analysis: pure Epoxy material 561 and epoxy with the following admixtures: MoO_3, Roflam P and Melamine, as well as 2 types of polyurethane form.

Keywords: fire, toxic products, smoke, visibility, evacuation.

1. Introduction

The knowledge of fire growth dynamics in a building is a base of fire safety evacuation. The time after which environment conditions of the building become critical is a fire-safety benchmark. The critical conditions of smoke filling, toxicity and thermal influence of the building environment should not exceed the necessary time allowing a safe evacuation of people from fire area.

The Interpretative Document 2 of the EU Council Directive 89/106/EEC defines basic requirements for fire safety which have to be met by buildings. Pursuant to the above EU law, specific fire protection regulations are set up individually in particular member states. Regulations referring to fire safety, currently valid in Poland and many other countries, do not limit the quantity of inflammable materials applied in compartments (excluding warehouses and public utility houses, i.e. rooms for more than 50 people). The inflammable components of interior equipment (e.g. furniture), as well as construction materials, including various systems, are the main source of large volume smoke production in the initial stage of a fire, the cause of visibility reduction and toxic influence on the occupants.

According to fire statistics, 80% of lives are taken because of the smoke presence (Clarke 1984). Smoke as the basic heat conveyor in a fire poses a major threat for people because of: inhalation of toxic substances which are integral part of it and attenuation of fire spaces and neighbouring enclosures. Both threats simultaneously cause problems with orientation to occupants and consequently render evacuation more difficult.

The object of this study is the analysis of promptness to reach critical conditions in the environment while burning selected interior finishing materials and equipment at set compartments volumes.

A simple model was presented to allow making a comparison of the influence of different combustibles on the time to reach untenable (critical) conditions. Simplicity of the model was based on the assumption of good mixing of combustion products with air as a consequence of turbulent movement in conditions of relatively low buoyant force (low value of Richardson's number) in volume of the room interiors. An advantage of a model that uses relatively simple mathematical dependencies is that it allows monitoring the impact of diverse parameters that characterise materials on time in which critical conditions are reached.

Naturally some models describe precisely and in greater detail the fire environment including ASET calculations. They take into account the chemistry of combustion processes and the complex structure of a fire including heat and mass exchange. Development of fire modelling in the past 30 years allowed the establishment of such complex zonal fire models as CFAST (National Institute of Standard and Technology/USA) (Jones et al. 2006) or such field models as FDS (NIST/USA) (McGrattan 2006), SMARTFIRE (University of Greenwich/UK) (Galea *et al.* 2007) and others.

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Epoxy materials, which are in common use, among others in construction, were used for research. For needs of fire protection modification used were additive fire retardants, which according to literature (Aseeva, Zaikov 1986; Troitzsch 1998; Levchik *et al.* 2005; Półka 2003) have inhibitory action mainly in the solid phase (MoO_3) and/or the gaseous one (melamine, Roflam P).

This study is a continuation of research executed by the Main School of Fire Service on evacuation rules and development of fire (Konecki, Półka 2006; Konecki 2006).

The results of fire parameters calculations and time to reach critical environment conditions due to toxic products and the range of visibility reduction are described in the article. The calculations were carried out with the visibility and toxicity analytical model using some of the experimental data of the materials (the fire properties of the materials).

2. Safe evacuation conditions in building fires

The influence of a fire on occupants during the first phase of a fire, when temperature of gaseous products outside the combustion zone is still low, is mainly connected with visibility limitations as well as irritating and narcotic features of smoke in a fire compartment, neighbouring enclosures and on evacuation routes.

The main factors of life threat are:

- The visibility limitation;
- Increase of carbon monoxide and dioxide
- concentration and other toxic and narcotic gases;
- Toxicity of gaseous products of combustion increasing along with the temperature, which physically affect the skin and respiratory tract;
- Depleting of oxygen concentration.

At the first stage of a fire, which is called the fuel controlled phase (pre-flashover phase), oxygen concentration could decrease to 18% which triggers diminishing the carbon dioxide concentration. Simultaneously carbon monoxide, nitrogen oxide, cyanide-hydrogen, small particle hydrocarbon CH_4, CH, formaldehyde and other highly irritating and asphyxiating compounds are generated.

A change in the range of visibility and toxic gases concentration, which influences the evacuation capability of occupants during a fire depends on the type of the fire and in particular on its growth rate characterized by heat release rate of inflammable materials $\dot{Q}$. Under conditions of a real fire the dangerous factors described above are not only determined by inflammable materials ($\dot{Q}$ value), but also characterize means of prevention and protection from fire occurring and spreading.

Coexistence of visibility limitation and toxicity phenomenon mechanisms is very complex. Most researchers (Rasbash, Drysdale 1982; Mulholland 2002; Babrauskas, Mulholland 1988; Baubrauskas 1972) believe in the synergetic effect of the above-mentioned threats concerning thermal conditions in a fire environment and above all the huge oxygen shortage resulting in creation of complex compounds which enhance toxic activities of several gaseous products of combustion and exhausts generated in fires.

Owing to the complex nature of this processes, the effect of inhaling toxic compounds generated during a fire and change of visibility are analyzed separately.

When taking life hazard of occupants into consideration, the fundamental criterion for life safety is fulfilled when possible evacuation time (Available Safe Egress Time – ASET) is longer than the required evacuation time (ISO/TS 13571 2002; Kosiorek 2004).

The possible evacuation time is a time interval between the onset of the fire (ignition of material) and the moment when the environment conditions reach the critical level, and therefore make the evacuation difficult and a direct health and life threat for the occupants arises. The critical states are frequently triggered off by limitation in the visibility range caused by smoke and exceeding the normal concentration of gaseous products of thermal decomposition and combustion.

Preliminary calculations related to the influence of various factors on the possible evacuation time are presented in the publication (Konecki 2006).

As regards the critical factors considered in this study, the critical time is usually shorter due to time-lag caused by the fire signalling activation.

With respect to what was said earlier, the condition of safety for occupants during evacuation is met when:

$$t_{cr} > t_{req} - t_{sign} , \qquad (1)$$

where t_{cr} – time after which fire critical parameter (dangerous factor) is reached (ASET), t_{sign} – time after which fire signalling is activated, t_{req} – required time of evacuation being a sum of times, when the evacuation was undertaken and time necessary to reach a safe location by people.

3. Increase of toxicity

In the first phase of a fire thermal decomposition products are supplied to the combustion zone mainly as a result of turbulent diffusion. The burning process is a result of radiant flux coming from the flame and impinging on a surface of a material. This causes an intensification of the burning process and consequently a rapid increase of carbon dioxide concentration. As a result of energy feedback, further destruction of thermal decomposition products within the flame zone takes place.

The efficiency of the burning process has an influence on toxicity of gaseous environment in a fire (Purser 1995). Smoke characterized by small optical density as well as complete oxidation of thermal decomposition products result in relatively small toxicity of the environment. The average gas temperature in a compartment (outside the burning zone) at the early stage of a fire is relatively small and reaches 100^0C.

While oxygen concentration decreases to 10–15% (in small rooms – 20 m^3), the concentration of CO could amount to ca. 1% and CO_2 to 10%. During the initial stage of a fire the CO_2 concentration increases rapidly, and then as a result of air lessening, it decreases to a low concentration (the CO_2/CO ratio is 1000/50). In small enclosures having a volume of approximately 100 m^3, the time after which a person looses consciousness due to intensive smoke and heat generation is only a few minutes.

Hazard connected with oxygen depleting occurs when its concentration (volumetric) drops below 21%. Products of deficient combustion, such as soot or aromatic hydrocarbons, can cause significant destruction of diverse objects. Soot particles which absorbed such gases as HCl, HBr, HF settle on surface of equipment causing corrosion. Combustion products like CO, HCN, CO_2 (in substantial concentrations) have a narcotic influence on people, and lead to loss of consciousness, which renders evacuation impossible and can cause even death.

Oxygen transport in animal organisms (also in human ones) is conducted by oxy haemoglobin (O_2Hb). Introduction of CO which has over 240 times greater affinity for joining with haemoglobin than oxygen, causes creation of carboxyhaemoglobin (COHb), which renders the transport of O_2 impossible. HCN also affects the cells causing a counteraction of oxygen transport. Studies executed to date allow the presumption that HCN is more toxic than CO. HCN acts through the concentration, whereas CO through the dose (quantified in simple terms as a product of the concentration and time, or, more accurately, as the COHb level that can be calculated, e.g. by the Steward's formula) (Purser 1995).

4. Visibility reduction

People most frequently suffer from limited visibility before the toxic and thermal impact of smoke begins to pose actual danger. The limited visibility range makes evacuation and fire extinguishing more difficult. The possibility of moving within the area of a fire mitigates the feeling of danger, and helps in improving efficiency and in avoiding panic.

The light on the way between people's eye and the observed object is scattered and absorbed by smoke particles.

Limitation of preliminary light intensity from I_0 to I after crossing the area filled with smoke on an optical distance L can be described by the well-known Bougher-Lambert-Beer equation:

$$I = I_O \exp(-K_S \cdot L), \tag{2}$$

where K_S is an extinction coefficient [m^{-1}] that is directly proportional to the concentration of smoke particles and its ability to scatter and absorb light.

The range of visibility Z is the largest distance from which the given object can be still seen in a smoke filled space and is inversely proportional to K_S (Rasbash, Drysdale 1982):

$$Z = \frac{C}{K_S}, \tag{3}$$

where C has a constant value, which is different for the object that reflects the light and that which shines suitably C = 2.3 and C = 5.8 (Rasbash, Drysdale 1982) and according to the latest version of the SFPE handbook of Fire Protection Engineering (Mulholland 2002), C = 3 for light-reflecting signs and C = 8 for light-emitting signs. For further comparative calculations C = 3 has been adopted.

According to the Polish standard PN-89/B-02856 (PN-89/B-02856, 1989) that uses the so-called NBS Smoke Chamber, the generation of smoke from materials is described by the maximal value of light attenuation coefficient Y_m and the rate of change $\dot{Y}_m$. These coefficients are directly connected with the range of visibility reduction.

The expression obtained on the assumption that $Y_m = \dot{Y}_m \cdot t$ allows calculation of the minimal range of visibility for homogenic smoke filling the inner space of a building with a given volume V (Sychta 1985):

$$Z = \frac{C \cdot V}{m_f \cdot \dot{Y}_m \cdot t}, \tag{4}$$

where t is the time needed to burn mass m_f of a given material.

In simultaneous combustion of n different materials, the range of visibility is described by the following dependence:

$$Z = \frac{C \cdot V}{t \cdot \sum_{i=1}^{n} m_{i,f} \cdot \dot{Y}_m^i}, \tag{5}$$

where $m_{i,f}$ is the mass of 'i' material, $\dot{Y}_m^i$ is the maximal change rate of contrast attenuation coefficient for 'i' material.

A study of smoke generation characteristics of interior finishing and furnishing materials has shown that most of them are highly smoke emissive, which is of great significance as it comes to the rate of visibility limitation during fires.

The critical values of the visibility range are shown in Table 1.

Table 1. The minimal range of visibility and acceptable smoke density obtained for safe evacuation purpose (Jin 1978)

Familiarity of the building	Range of visibility Z [m]	Smoke density Extinction coefficient K_s [m^{-1}]
Known building	3–5	0.4–0.7
Unknown building	15–20	0.1

Recently published data in the standard PD7974 (PD7974-6 2004) specify critical values of the visibility range: for small enclosures and travel distances – 5 m and for the large enclosures and travel distances – 10 m.

The critical ranges of visibility used in calculations were 5 m and 10 m.

5. Conservation laws for control volume

Conservation of mass

The conservation law for control volume for discrete regions of mass exchange "j" can be expressed as

$$(\dot{m})_V + (\sum_{j=1} \dot{m}_j)_{out} - (\sum_{j=1} \dot{m}_j)_{in} = 0\,, \tag{6}$$

where the sum describes all flows from and to the control volume V.

Conservation of mass for reacting species

The conservation law can be presented in a form for room fires with zone uniform structures:

$$(\dot{m}_j)_V + \sum_{j,netout} \dot{m}_{i,j} + \sum_{j,netout} \dot{m}_{i,d,j} = \dot{m}_{i,r}\,, \tag{7}$$

where $\dot{m}_{i,j}$ represents the bulk flow rate of species “i”, $\dot{m}_{i,d,j}$ is the diffusion flow rate at each flow path. For the uniform concentration case (the concentrations of species Y_i are uniform throughout the control volume) the mass of species $m_i = mY_i$, where m is the mass in the control volume and Y_i designed the mass fraction of species “i”.

The more useful form of equation (7) can be obtained by multiplying equation (6) by Y_i

$$\frac{dmY_i}{dt} + \sum_{j,in} \dot{m}_j (Y_i - Y_{i,j}) + \sum_{j,out} \dot{m}_{i,d,j} = \dot{m}_{i,r}\,, \tag{8}$$

where $Y_{i,j}$ represents the mass fraction for each species “i” at entering “j” flow paths.

The total combustion reaction in fire can be described by the chemical equation as:

$$\begin{aligned} &\phi n_f C_m H_n O_p N_g Cl_f + n_1 (O_2 + 3{,}76 N_2) \rightarrow \\ &n_2 CO_2 + n_3 CO + n_4 H_2O + n_5 HCl + n_6 HCN + \\ &3{,}76 n_1 N_2 + n_7 S(smoke) + n_8 C_x H_y, \end{aligned} \tag{9}$$

where ϕ is the equivalence ratio described as $\phi = \dfrac{mass \cdot of \cdot fuel \cdot available}{mass \cdot of \cdot oxygen \cdot available} / r$, r is the stoichiometric value for complete combustion, n are the stoichiometric coefficients. Usually the smoke is assumed as pure carbon (soot) (Quintiere 2006).

The mass balance statement for the mass rates can be shown as:

$$\begin{aligned} &\dot{m}_f + \dot{m}_{O_2} = \dot{m}_f + \dot{m}_f \cdot \frac{\Delta h_c}{E} - \dot{m}_f \cdot \left(\frac{O_2}{f} \right) = \\ &\dot{m}_{CO_2} + \dot{m}_{CO} + \dot{m}_{H_2O} + \dot{m}_{HCl} + \dot{m}_{HCN} + \dot{m}_S + \dot{m}_{C_X H_Y}\,, \end{aligned} \tag{10}$$

where E is the heat release per mass unit of oxygen consumed is fairly constant as 13.0 ± 0.3 MJ/kg for various fuels (Huggett 1980). Δh_c the heat of combustion, O_2/f is the mass ratio of oxygen to the fuel.

Another way is to introduce y_{0_2}, oxygen requirement describing oxygen mass in kg necessary to complete combustion of 1 kg of material.

The mass rates for each species „i” $\dot{m}_i$ are expressed using the yields y_i and $\dot{m}_f$ as:

$$\dot{m}_i = y_i \cdot \dot{m}_f\,, \tag{11}$$

$$y_i = \left(\frac{n_i}{n_f} \right) \left(\frac{M_i}{M_f} \right) \text{ and } \sum_i y_i = 1\,, \tag{12}$$

where n_i i n_f are the stoichiometric coefficients, M_i and M_f molecular weight of a molecule „i” and molecular weight of a fuel.

For fuels that completely gasify to the same chemical state as in a phase change for a pure substance, the yield is equivalent to the stoichiometric coefficient. For complex fuels (for example, wood, charring materials) which only partially undergo pyrolysis and the gaseous products are no longer the fuel chemical, we cannot equate yield to a stoichiometric coefficient. The use of the mass rate of production of species “i” is practical and necessary in characterizing such fuels.

Conservation of energy

For a perfect gas mixture with uniform properties in the control volume we can assume

$$c_p m \frac{dT}{dt} - V \frac{dp}{dt} + c_p \sum_{j,in} \dot{m}_j (T - T_j) = \dot{m}_f \Delta h_c + \dot{Q}_{net} - \dot{W}, \tag{13}$$

where T is the uniform temperature in the control volume, T_j – the temperature of “j” flow, $\dot{m}_f$ – the mass consumption rate of the fuel and $\dot{Q}_{net}$ describe the net rate of heat. c_{pi} is the specific heat of species “i”, p – the pressure, $\dot{q}''$ – the rate of heat added to the control volume, Δh_c – the effective heat of combustion, $\dot{m}'''_f$ – the mass consumption rate of the fuel per unit volume, W – net rate of shaft and shear work done by the fluid in the control volume, N – the number of species.

The decomposition of solid polymer to produce pyrolysis products that contain gaseous fuel and smoke particles. The consumption rate of the fuel $\dot{m}_f$ is a function of chemical decomposition kinetics, heat conduction, charring and possibly other physical, chemical and thermodynamic properties of material.

6. The assumptions of fire model

Equations (6), (8) and (13) could be useful in describing the conservation laws for the zone structure in compartments fires. A control volume can be selected as the smoke layer under ceiling (classical two-zone model) or the entire volume of the compartment (one-zone model).

One-zone models have been widely used in analyses of post-flashover fires since the 1970-ies (Babrauskas, Wiliamson 1978; Lathan *et al.* 1987; Buchanan 1998; Cadorin, Franssen 2003; Utiskul 2007 *et al.*). In this fire phase flames and smoke fill the entire interiors of premises. The heat generation rate in a room depends on ventilation conditions. This state is generally known as ventilation limited.

Two-zone approximations are primarily used to describe a fire environment in the phase of its growth (pre-flashover phase of fire), in which the flames (combustion zone) have been located, and smoke accumulates under the ceiling slab of the interior, forming the upper hot layer. Below is the cool bottom layer, with low contamination by combustion products.

In this study the one-zone model approach was used to describe pre-flashover fires. This approximation may be correct provided that one of the additional assumptions related to fire spreading is fulfilled (Quintiere 2006), such as:

- smoke movement in the compartments is remote from the fire room,
- heat generation rate from the given material is relatively low and does not cause generation of sufficiently big buoyant forces to allow creation of well defined top smoke layer,
- mixing processes occur caused by flows of the gaseous phase in complex internal spaces of premises (such as partition walls, columns etc).

In all the above specified cases assumed is a sufficient oxygen volume in the surroundings of the combustion zone – small combustion zone and large spaces inside the building (special case of well ventilated fire).

The simple hand method, described below, is particularly useful for comparative studies of the impact of properties of materials having different composition in the generation rate of the fire environment.

In other words, it is useful for assessing the safety of evacuation in a fire environment in large interior spaces of building.

As data obtained on a small scale have been used for calculations (Cone Calorimeter, NBS Smoke Chamber), where a sample of material with constant surface was burnt, also assumed was a constant combustion surface of materials in room interiors (the flame spreading rate was equal to zero) of 1 m^2.

The fundamental additional assumptions are:

- complete combustion,
- constant fire area (combusted material),
- constant mass combustion rate of a material,
- chosen most dangerous species are under consideration (calculated separately),
- no chemical kinetics,
- uniform average gas density in the compartment,
- no inside flow of ‘i’ product of combustion and small outside flows (the leakages).

The partial conservations of mass for species, smoke and fuel can be expressed from equation (8) as

$$\frac{dmY_i}{dt} + \sum_{j,in} \dot{m}_j (Y_i - Y_{i,j}) + \sum_{j,out} \dot{m}_{i,d,j} = \dot{m}_i , \tag{14}$$

$$\frac{dmY_S}{dt} + \sum_{j,in} \dot{m}_j (Y_S - Y_{S,j}) + \sum_{j,out} \dot{m}_{S,d,j} = \dot{m}_S , \tag{15}$$

$$\frac{dm_f}{dt} = -\dot{m}_f , \tag{16}$$

$$\dot{m}_i = y_i \cdot \dot{m}_f , \quad \dot{m}_S = y_S \cdot \dot{m}_f , \; \dot{m}_{O_2} = y_{O_2} \cdot \dot{m}_f . \tag{17}$$

Species

Mass conservation equation for ‘i’ gaseous product in the compartment, the volume of which is V, can be obtained from the equation (14) as:

$$\frac{d}{dt}\left(V\rho Y_i\right) = \chi \dot{m}''_f A_s y_i - \dot{m}_{out}\, Y_i , \tag{18}$$

where ρ is the average gas density in the compartment (kg/m^3), Y_i describes concentration of ‘i’ component (CO$_2$, CO, HCl, HCN) formulate by mass fraction (-), $\dot{m}''_f$ is the mass consumption rate (in well-ventilated fires it equals to the mass combustion rate) of the fuel per unit area (kg/m^{2}s), where $\dot{m}''_f = \dot{m}_f / A_s$, A_s is the constant area of combusted material which equals 1 m^2 (in compliance to the assumptions of fire model), $\dot{m}_{out}$ – the mass flux emerging from a compartment (kg/s), y_i – the emission of ‘i’ component (–), and χ combustion efficiency coefficient equal to 1. By integrating the equation (15), the following expression is obtained:

$$Y_i = \frac{\chi \dot{m}''_f A_s y_i}{\dot{m}_{out}} \left[1 - \exp\left(-\frac{\dot{m}_{out}}{V \cdot \rho} t \right) \right]. \tag{19}$$

For the low ventilation conditions – small $\dot{m}_{out}$ (and also constant density ρ) obtained expression describes the time of critical concentration t^i_{cr} by the ‘i’ product:

$$t^i_{cr} = \frac{V\rho}{\chi \dot{m}''_f A_s y_i} Y^i_{cr} . \tag{20}$$

Smoke

In the equation (16) instead of the mass rate for smoke $\dot{m}_S$, the maximal value of light attenuation coefficient Y_m, connected with the visibility range, can be introduced as follows:

$$\frac{dmY_S}{dt} = \dot{m}_S = \frac{Y_m}{\alpha} \dot{m}_f , \tag{21}$$

Y_m is defined in terms of the yield of soot (y_S) as $Y_m = \alpha y_S$, where α is termed the aerosol particle optical density, which is constant for flaming smoke (Rasbash, Drysdale 1982).

The concentration of smoke particles Y_S can be expressed in terms of optical properties defined by an extinction coefficient K_S as $Y_S = K_S / \alpha\rho$ (Sychta 1985).

Using the equations (3), (21) and above definitions, it was possible to describe the most dangerous smoke conditions in the compartments with applying the constant value $\dot{Y}_m$. This parameter is connected with maximum rate of smoke emission from materials in fire environment (Sychta 1985) and generally

$$Y_m = \int_0^t \dot{Y}_m dt .$$

The time, after which the range of visibility reaches its critical value, can be expressed by the equation (4) as:

$$t^S_{cr} = \frac{C \cdot V}{\dot{m}''_f \cdot \dot{Y}_m \cdot Z_{cr}} . \tag{22}$$

Energy

The conservation of energy for the zone is applied together with equations of mass and species and the equation of state as:

$$c_p\rho V\frac{dT}{dt}-V\frac{dp}{dt}+c_p\sum_j \dot{m}_j(T-T_j)=\dot{Q}-\dot{Q}_{loss}\,, \quad (23)$$

where p – the pressure in the enclosure is considered uniform in the energy equation, $\dot{Q}$ is the rate of heat release from the fuel, $\dot{Q}_{loss}$ – the rate of heat transfer lost at the boundary.

For compartments with leaks the pressure rise is usually insignificant and the pressure remains nominally practically at ambient pressure.

In the Eurocode norms (BS 7974: 2003, Eurocode 1: 2002), applying to various purposes of fire safety, the increase of the heat generation rate is described by the dependence $\dot{Q}=\alpha t^2$, in which for the α coefficient values were adopted that range from 0.19 *kW/s*^{2} for very quickly spreading fires, to very slowly spreading ones for which $\alpha = 0{,}003 kW/s^2$.

Studies of fire dynamics at the beginning of the pre-flashover phase for diverse lining materials of mattresses subject to combustion from relatively small fire sources (a few kW) in a horizontal position towards the floor indicate values of α within the range of 0.0002 to 0.001 kW/s^2 (Schifility *et al.* 2002; Konecki 2006).

Assuming a fire source as a function of time $\dot{Q} = \alpha t^2$ for value α = 0.001 kW/s^2 for the fires mentioned above with $\dot{Q}_{loss} = 0$ in the enclosure volume V = 3000 m^3 with leakiness, we obtain from equation (23) the average temperature raise ΔT = 130 °C after time of combustion equal to ca. 13 min.

Calculations described above allow the assumption that ρ is approximately an average constant value for a relatively long period of time. Adoption of lower α values would obviously extend that time.

7. Experiment

7.1. Description of experimental materials

The study was conducted with the use of polymers, which have common application as interior finishing, furnishing and isolation materials with various thermokinetic, smoke generation and emissive characteristics (Table 2).

The experiment materials were described below:

- unmodified epoxy materials (without flame retardant) made from epoxy resin – Epidian 561,
- epoxy materials made from resin (Epidian 561) with fire retardants – MoO_3, Roflam P and melamine,
- polyurethane foams – two kinds.

The samples of epoxy resin unmodified and one with fire retardants were produced by “Organic Sarzyna” Polish Chemical Corporation. Epidian 561 is a coloured two-component (A and B) poured out flooring composition:

Component A – unmodified epoxy resin Epidian 561 containing inorganic pigments and fillers (32% by weight, dense mass) or modified resin with fire retardants – 8% (by weight) molybdenum oxide (VI) or 8% (by weight) melamine or 5% (by weight) Roflam P.

(Molybdenum oxide MoO_3 (VI), melamine – produced by POCh, Gliwice, Poland).

Roflam P is the trade name of flame retardant produced by the Polish Chemical Corporation PCC Rokita. It is tri(2-chloro-2-methylethyl) phosphate.

Table 2. Thermokinetic behaviour of selected materials. Well–ventilated fires, the equivalence ratio ϕ <1. The main findings obtained from the cone calorimeter (ρ – density, Δh_c – average effective heat of combustion, $\dot{m}''_f$ – average mass combustion rate, $\dot{Q}''$ – heat release rate per unit area

Material	ρ [kg/m^3]	Δh_c [MJ/kg]	$\dot{m}''_f$ [kg/m^{2}s]	$\dot{Q}'' = \Delta h_c \cdot \dot{m}''_f$ [kW/m^2]
Epoxy material 561	1413	44.00	0.017	748
Epoxy material 561 + 8% MoO_3	1407	39.44	0.012	473
Epoxy material 561 + 5% RoflamP	1432	38.80	0.015	582
Epoxy material 561 + 8% Melamine	1383	42.,30	0.011	465
Polyurethane foam I	35	27.20	0.010	272
Polyurethane foam II	30	26.80	0.011	295

Component B – modified aliphatic polyamine – Hardener ET (low viscous liquid, quantity of hardener for 100 g of Epidian 561 was 10 g).

The coating thickness of samples of Epidian 561 with or without flame retardants with hardener ET was 3 to 5 mm. The gel time (sample 100g at temperature 20 °C) was ca. 35 minutes. The viscosity of mixture at a temperature of 25 °C was 1000 to 2500 mPa.

The modified epoxy resin with inorganic pigments, fillers and flame retardants showed a higher density mass. Epidian 561 is an epoxy composition with good mechanical and chemical resistance recommended for pouring out flooring on concrete foundation in industrial buildings.

In the studies use was made of hardened non-modified samples of Epidian 561 or with fire retardants in the form of cast profiles with dimensions of 10×10 [cm].

Polyurethane foams used in the studies were taken from a car seat (foam I) and furniture upholstery (foam II). Requirements for foam as car seat is described as: hardness 155 to 185 [N], endurance ≥8 [N/cm^2], elongation ≥100 [%], density 35 [kg/m^3].

The density of furniture upholstery foam was 30 [kg/m^3].

7.2. Test methods and experimental data

The cone calorimetric method for determining average mass combustion rate, average effective heat of combustion and emissions of chosen combustion products have been used (ISO 5660 1991). For further calculations the average value of mass combustion rate per unit area $\dot{m}''_f$ for selected materials have been taken into consideration. The average value of heat release rate per unit area $\dot{Q}''$ was calculated as a product of average mass combustion rate and average effective heat of combustion S. Generation of smoke from materials described by maximal value of light attenuation coefficient Y_m and the rate of change $\dot{Y}_m$ have been studied in the Polish standard PN-89/B-02856. This method is based on NBS Smoke Chamber where smoke is accumulated in a closed space. Smoke evolution was measured by a laser photometer. All experimental heat and smoke data were determined for external heat flux 50 kW/m^2. The smoke data described above were used to calculate the visibility range. The results of research have been presented in Table 2 and 3.

Table 3. Smoke behaviour and toxic products emission (yields) from selected materials. Well–ventilated fires, the equivalence ratio $\phi < 1$. $\dot{Y}_m$ – maximal value of rate of change of light attenuation coefficient obtained from PN-89/B-02856, y_{CO} – emission of CO, y_{CO_2} – emission of CO$_2$ obtained from the cone calorimeter

Material	$\dot{Y}_m$ [m^2/kgs]	y_{CO} [kg/kg]	y_{CO_2} [kg/kg]
Epoxy material 561	5.37	0.054	1.640
Epoxy material 561 + 8% MoO$_3$	2.71	0.049	1.760
Epoxy material 561 + 5% RoflamP	6.19	0.089	1.525
Epoxy material 561 + 8% Melamine	4.84	0.081	1.916
Polyurethane foam I	5.20	0.049	2.400
Polyurethane foam II	2.31	0.046	2.200

Data in Tables 2, 3 were obtained during combustion of materials in well ventilated conditions, i.e. conditions similar to the one at the very beginning of a fire, where the rate of combustion depends only on spatial orientation and composition of a material. A comparison (Table 2) of the heat release rate per unit area for epoxy 561 materials with data for material with admixtures confirms the fire resistance of the applied substances. As regards MoO$_3$, the value of $\dot{Q}''$ was reduced by 37%, RoflamP by 22% and Melamine by 38%. For comparison, the average value of $\dot{Q}''$ for wood amounts to ca. 100–150 kW/m^2 (Baubrauskas, Grayson 1992; Babrauskas 2005).

Relatively low values of maximum smoke emission rates (low $\dot{Y}_m$ values) from studied materials have been obtained with respect to flameless combustion with thermal radiation flux within the range of 20 to 30 kW/m^2.

As regards the admixture of RoflamP, an increase of smoke emission occurs as compared to pure material, which arises from the presence of chlorine in the retardant. The addition of Melamine causes a relatively insignificant lowering of smoke emission, as compared to Epoxy material 561. Reduction of smoke generation by 50% was found, when 8% MoO$_3$ was added to the material (Table 3).

Polyurethane foams with similar CO and CO$_2$ emissions differ as regards smoke generation (Table 3).

An increase of CO emission with Epoxy material was observed after addition of RoflamP and Melamine, contrary to MoO$_3$ in the case of which the change was insignificant (Table 3). Furthermore, the addition of MoO$_3$ and Melamine led to higher CO$_2$ emission, and if RoflamP is added, its reduction (Table 3).

The data were used to calculate toxicity and visibility reduction. During combustion of most studied materials the danger of reduction of oxygen concentration occurs after a long period of combustion (Konecki, Półka 2006; Konecki 2006). Because of it depletion of oxygen have not been discussed here. Owing to lack of data concerning HCN emission for the studied polyurethane foams, no calculations were carried out for that product.

8. The critical time calculations

It was assumed that 1 kg of interior finishing material was subjected to complete combustion in well ventilated compartments (cubages of compartments – 1000 m^3 and 3000 m^3 with leakiness – there is no air flow into the enclosure and only a small amount of smoke emerges outside) with infinitely fast flaming ignition and constant rate of combustion. This enclosure would be a model interior space approximate to the rectangular prism, the height of which of ca. 3 m is typical for the regular office or residential compartment. It was also assumed that gaseous phase is mixing well and has constant density which is proven by a minor increase in gas temperature.

The following critical values of combustion products concentration were assumed for a situation, where loss of consciousness of 50% of the population after 30 min of exposure is observed (Purser 1995):

$$Y_{cr}^{CO} = 1.5\text{x}10^{-3}\ \text{kg/kg},$$

$$Y_{cr}^{CO_2} = 7.5\text{x}10^{-2}\ \text{kg/kg}.$$

For smoke calculations, data from Table 3 were used. Adopted was the constant value of C = 3 that describes observation of light-reflecting signs (Mulholland 2002). Two criteria values for the range of visibility were assumed: $Z_{cr} = 5$ m and $Z_{cr} = 10$ m (PD7974-6, 2004).

The results of critical time taking into consideration visibility reduction have been shown in Table 4.

Time values which were received as compared to those for the range of visibility are relatively longer, especially for the compartments of a greater volume. Obviously critical times for the criterion value $Z_{cr} = 5$ m will be longer than for the criterion value $Z_{cr} = 10$ m for all cases. As was shown above (equation 22), the critical time of visibility reduction is connected with the maximal value of change rate of light attenuation coefficient $\dot{Y}_m$ and the average mass combustion rate $\dot{m}''_f$.

Table 4. Critical times of the visibility limitation for selected materials in different enclosures of building

Material	The compartments volume $V = 1000$ m^3	The compartments volume $V = 3000$ m^3
Epoxy material 561	t_{cr} (5 m) = 109 min t_{cr} (10 m) = 55 min	t_{cr} (5 m) > 5 h t_{cr} (10 m) = 165 min
Epoxy material 561 + 8% MoO_3	t_{cr} (5 m) > 5 h t_{cr} (10 m) = 154 min	t_{cr} (5 m) > 15 h t_{cr} (10 m) > 7 h
Epoxy material 561 + 5% RoflamP	t_{cr} (5 m) = 108 min t_{cr} (10 m) = 54 min	t_{cr} (5 m) > 5 h t_{cr} (10 m) = 162 min
Epoxy material 561 + 8% Melamine	t_{cr} (5 m) > 3 h t_{cr}(10 m) = 94 min	t_{cr} (5 m) > 9 h t_{cr} (10 m) > 4 h
Polyurethane foam I	t_{cr} (5 m) > 3 h t_{cr} (10 m) = 96 min	t_{cr} (5 m) > 9 h t_{cr} (10 m) > 4 h
Polyurethane foam II	t_{cr} (5 m) > 6 h t_{cr} (10 m) >3 h	t_{cr} (5 m) > 18 h t_{cr} (10 m) >9 h

The calculated values should be treated as minimal because in the standard conditions of building environment there is an air flow coming in from the outside of the compartment and dissolving emerging smoke, as well as simultaneously emerging thermal decomposition and combustion products from vent openings (e.g. windows). Critical times of the visibility limitation (for compartments with a volume $V = 1000$ m^3 and $Z_{cr} = 10$ m) are from 54 min. to 154 min. for epoxy materials and from 96 min. to above 3 hrs for polyurethane foams. These times were adequately longer for compartments with a volume of $V = 3000$ m^3 and the criterion $Z_{cr} = 5$ m. Results of calculations indicate considerable extension of the critical visibility time during thermal decomposition and combustion of Epoxy material with MoO_3 and Melamine. The admixture of RoflamP does not change the time, in which critical visibility is reached (Table 4).

To assess the rate of toxic threat occurrence after thermal decomposition of materials in well ventilated compartments of given volumes (the large volumes compartments with small gap where there is no air flow into the compartment and only small quantities of smoke emerge outside). The critical times of the materials have been listed in Table 5. Calculations, which are to determine the time until critical state of a building, when it starts to pose danger for occupants with respect to environment toxicity, were made with the use of dependence (20). Rapid increase in environment toxicity due to combustion product emission (CO) from chosen materials in the range of 19 min. – 51 min. (the compartments volume $V = 1000$ m^3) should be emphasized. These characteristics arise primarily from the greatest combustion rates and consequently the greatest heat emission of these materials (Table 2). In spite of the emissions of CO_2 are about 30–50 times higher than emissions of CO, critical states of CO were achieved earlier. This was related to the difference in critical values of combustion products concentrations.

Table 5. Critical time calculations results considering toxic products

Material	The compartments volume $V = 1000$ m^3	The compartments volume $V = 3000$ m^3
Epoxy material 561	$t_{cr}^{CO} = 27$ min $t_{cr}^{CO_2} = 45$ min	$t_{cr}^{CO} = 81$ min $t_{cr}^{CO_2} = 135$ min
Epoxy material 561 + 8% MoO_3	$t_{cr}^{CO} = 43$ min $t_{cr}^{CO_2} = 59$ min	$t_{cr}^{CO} = 129$ min $t_{cr}^{CO_2} = 177$ min
Epoxy material 561 + 5% RoflamP	$t_{cr}^{CO} = 19$ min $t_{cr}^{CO_2} = 55$ min	$t_{cr}^{CO} = 57$ min $t_{cr}^{CO_2} = 165$ min
Epoxy material 561 + 8% Melamine	$t_{cr}^{CO} = 28$ min $t_{cr}^{CO_2} = 59$ min	$t_{cr}^{CO} = 84$ min $t_{cr}^{CO_2} = 177$ min
Polyurethane foam I	$t_{cr}^{CO} = 51$ min $t_{cr}^{CO_2} = 52$ min	$t_{cr}^{CO} = 153$ min $t_{cr}^{CO_2} = 156$ min
Polyurethane foam II	$t_{cr}^{CO} = 49$ min $t_{cr}^{CO_2} = 52$ min	$t_{cr}^{CO} = 147$ min $t_{cr}^{CO_2} = 156$ min

9. Discussion of results

In this study measurements were made of changes in toxicity and smokiness of the environment in enclosures which result from fires taking place in public premises. It was confirmed quantitatively that smoke and toxic gases are the most influencing factors when it comes to possible evacuation time of occupants from the building. Thermal decomposition and combustion products of interior finishing, furnishing and isolating system materials influence adversely the evacuation process of occupants or movement on the general communication routes that serve as evacuation routes.

Hence the proper selection of interior finishing materials plays an important role in designing evacuation routes.

Tables 6 and 7 list the minimal critical times taking into account the toxic products generated during decomposition and combustion of investigated materials and the range of visibility.

The appearance of a critical state during a compartment fire of chosen materials is connected with a critical visibility range and consequently critical concentrations occurrence by CO, which confirm the study done so far on materials of varying chemical composition (Jin 1978; Purser 1995; Konecki 2006).

As shown above in Table 6 for epoxy materials, the critical state of toxicity (CO) is obtained within a time which is 2 to 3.5 times shorter than the critical state of visibility. Addition of Melamine and MoO_3 retardants causes ASET increases as compared to Epoxy material 561. As regards RoflamP, its decrease occurs.

Table 6. Minimal critical time (ASET – available safe egress times from compartments) considering toxic products and visibility range during the combustion of epoxy materials

Material	The compartments volume V = 1000 m^3	The compartments volume V = 3000 m^3
Epoxy material 561	t_{cr}^{CO} = 27 min t_{cr}(10 m) = 55 min	t_{cr}^{CO} = 81 min t_{cr}(10 m) = 165 min
Epoxy material 561 + 5% RoflamP	t_{cr}^{CO} = 19 min t_{cr}(10 m) = 54 min	t_{cr}^{CO} = 57 min t_{cr}(10 m) = 162 min
Epoxy material 561 + 8% Melamine	t_{cr}^{CO} = 28 min t_{cr}(10 m) = 94 min	t_{cr}^{CO} = 84 min t_{cr}(10 m) = >4 h
Epoxy material 561 + 8% MoO_3	t_{cr}^{CO} = 43 min t_{cr} (10 m) = 154 min	t_{cr}^{CO} = 129 min t_{cr}(10 m) > 7 h

Epoxy material modified by the applied flame retardant RoflamP manifests a higher CO and smoke release, as compared to Epidian 561 with fire retardants – MoO_3 and Melamine. This is connected with the presence of chlorine atoms as a component of RoflamP, which apart from acting as an anti-flammability agent during thermal decomposition and combustion also emits a gaseous HCl that acts as inhibitor for the flammable gaseous phase and formation of aromatic structures causing increased generation of smoke particles.

In spite of differences in the average mass combustion rates (Table 2) of Epidian 561 with fire retardants – MoO_3 and Melamine (epoxy resin with MoO_3 has a greater value of $\dot{m}''_f$), the critical state of visibility is obtained within a shorter time for Epidian with Melamine. The reason is that $\dot{Y}_m$ for epoxy material 561 with Melamine is about 1.8-fold higher than $\dot{Y}_m$ for epoxy resin with MoO_3 (Table 3).

CO emissions during combustion of foams are quite similar (Table 3). The same concerns mass combustion rates per unit area $\dot{m}''_f$. As an effect the calculated ASET for both types of foams, are comparable (Table 7). However, considerable differences have been obtained in values of critical times in reduction of visibility range. ASET for Polyurethane foam I is over twice lower than for Polyurethane foam II (Table 7). This is connected with differences in the maximal value of the change rate in light attenuation coefficient $\dot{Y}_m$ described for foams (Table 3). A similar dependence was also described for epoxy materials. A more intense generation of smoke particles from Polyurethane foam I may be explained by conditions of thermal decomposition (lower density of external heat flux).

Table 7. Minimal critical time (ASET – available safe egress times from compartments) considering toxic products and visibility range during the combustion of polyurethane foams

Material	The compartments volume V = 1000 m^3	The compartments volume V = 3000 m^3
Polyurethane foam II	t_{cr}^{CO} = 49 min t_{cr}(10 m) >3 h	t_{cr}^{CO} = 147 min t_{cr}(10 m) >9 h
Polyurethane foam I	t_{cr}^{CO} = 51 min t_{cr}(10 m) = 96 min	t_{cr}^{CO} = 153 min t_{cr}(10 m) >4 h

The obtained values should be treated as approximate and average. When describing smokiness and toxicity of gaseous environment in the compartments, the distribution of products concentration, thermal field variability, heat flux impinging on material and toxic products and synergism causing complex non-additive effects have not been taken into account.

The environment toxicity analysis of a full scale fire as well as the model calculations, which were carried out in the study, indicate there is a strong dependence between the dynamics of toxic product concentration and smokiness. The latter depends on chemical composition and molecular structure, mass, form and conditions of special orientation, thermal decomposition conditions, process of combustion and ventilation.

In this study we have examined the influence of particular conditions of a fire described by fire parameters on possible evacuation time. The time to reach the critical state for selected materials along with the simplification of smoke spreading and toxic products models in the low ventilated compartments were assumed. By doing so it was possible to make a supposition regarding conditions that pose the greatest danger for occupants of the said compartments. The intensification of toxic influence for thermal decomposition products and combustion (synergism) have not been taken into account.

Better safety conditions for evacuation of people may be assured as follows: smoke and fire limitation on evacuation routes through restriction in the use of highly flammable and smoke generating building materials, or retardation of combustion initiation and fire growth by implementing counter fire modification of materials.

10. Conclusions

Research executed to date by numerous authors implied that the rate of critical conditions occurrence taking toxic products and smokiness into consideration is a strong function of fire dynamics described by heat release rate, mass combustion rate, emission of mass flux of thermal decomposition products. Results gained over the period of the last 30 years indicate the existence of a significant relationship between the rate of toxic hazard occurrence, limitation of visibility and the chemical composition of combusted material.

This study presented a simple one-zone analytical model for comparative tests of critical times during combustion of polymer materials in confined spaces.

The basic advantage of the model is the possibility of monitoring the impact of various parameters that characterise materials on times of reaching critical conditions of visibility reduction and environment toxicity.

For needs of the analysis chosen were epoxy materials, which to date have not been extensively studied – pure Epoxy material 561 and the same material with admixtures: MoO_3, Roflam P and Melamine, and in addition two types of polyurethane foam.

The executed comparative studies allow making the following conclusions:

- Confirmation was found for action of MoO_3, Roflam P and Melamine admixtures to Epoxy material 561 as retardants – they lead to reduction of combustion rate and heat release rate (HRR) as compared to the material without modification. The strongest retarding action is manifested by MoO_3 and Melamine.
- Addition of RoflamP triggers increased smoke emission and reduction of visibility reduction critical time as compared to pure material, which is an effect of the presence of chlorine in the retardant. MoO_3 and Melamine reduce smoke emission and as a consequence also ASET increase.
- The addition of RoflamP or Melamine leads to increased CO emission from the epoxy material. Only in the case of RoflamP a reduction of ASET takes place as compared to pure epoxy material. Addition of MoO_3 leads to considerable extension of the critical time.
- The studied polyurethane foams indicate comparable CO and CO_2 emissions. Polyurethane foam I is characterised by higher smoke particle generation than polyurethane foam II, which arises from thermal decomposition conditions. Critical states for CO for both types of foams are attained after a similar time. The visibility range achieves critical values quicker during combustion of polyurethane foam I.
- For all the tested materials, the critical state of toxicity (CO) is obtained quicker than the critical state of visibility. This is primarily connected with relatively low smoke emissions characterised with the use of maximum values in the rate of contrast coefficient changes. Maximum smoke generation was ascertained during action of thermal radiation flux falling on samples of materials with respect to flameless combustion. A consequence of earlier reached CO risk condition than the visibility range reduction may be that owing to lack of awareness of CO exposure (smoke is visible and CO is naturally not) persons exposed to a longer stay in the fire environment risk dying.

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POLIMERINIŲ MEDŽIAGŲ DEGIMO SUPAPRASTINTAS GAISRO MODELIS LYGINAMOSIOMS KRITINIŲ SITUACIJŲ STUDIJOMS

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Santrauka

Laikas, reikalingas žmonėms evakuotis iš pastato (evakuacijos laikas), turi būti trumpesnis už laiką, per kurį konkreti pastato erdvė tampa pavojinga gyvybei (leistinas saugios evakuacijos laikas – angl. ASET). Šis laikas apibrėžia priimtinų dūmų plitimo, toksiškumo ir šiluminio poveikio pastato erdvei ribų viršijimą. Dėl dūmų žmonės praranda orientaciją, todėl evakuacija užsitęsia arba tampa neįmanoma. Dėl tokiomis aplinkos sąlygomis įkvepiamo didelio toksinų kiekio galima prarasti sąmonę ar net mirti. Straipsnyje apžvelgiama matomumo per dūmų sluoksnį ir toksiškų produktų koncentracijos įtaka evakuacijos laikui (ASET), kai degančioje patalpoje gaisro metu užtikrinama gera oro ventiliacija. Greta matomumo buvo tiriama CO ir CO_2 koncentracijos įtaka evakuacijos laikui. Pateiktos formulės rodo degimo intensyvumo ir dūmų bei toksiškų priedų išsiskyrimo įtaką matomumo mažėjimui ir toksinių produktų koncentracijos didėjimui įvertinant konkrečios medžiagos degimą. Tyrimams naudotos šios medžiagos: epoksidinė medžiaga 561 be priemaišų, epoksidinė medžiaga su MoO_3, Roflam P ir Melamine priedais, dvi poliuretano detalės.

Reikšminiai žodžiai: gaisras, toksiškieji produktai, dūmai, matomumas, evakuacija.

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