Phosphorus-containing flame retardants for fire-safe foamed polymers

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Abstract: The increased fire hazard of foamed polymers hinders their widespread use in the construction industry. An effective method of reducing the combustibility of carbonizing polymers is the use of phosphorus-containing flame retardants. Therefore, investigation of the influence of phosphorus-containing flame retardants to the composition of pyrolysis products and operational properties – heat resistance, flammability, combustibility and smoke generating ability – is the important objective. In the article we have presented the results of related experimental studies. The effects of phosphorus-containing flame retardants on heat resistance and main operational properties related to fire-safety of foamed constructional polymers are examined. A correlation was found between the results of evaluating the combustibility of foams by the limiting oxygen index and the combustibility index. Optimal concentrations of phosphorus in the foamed thermosetting polymers are established. It was shown that optimal concentration of the flame retardants leads to low combustibility of polyurethane-, resole- and urea-based foamed polymers.
Keywords: foamed polymers, fire hazard, reducing the combustibility, phosphorus-containing flame retardants, heat resistance, flammability, combustibility and smoke generating ability.

1. Introduction

As of current, energy saving and energy efficiency are the key economic problems in construction industry. These problems are of special importance in case of new industrial and residential buildings and structures, as well as when transporting the heat transfer agents from the manufacturer to the consumer [1]. Buildings may consume more than 50% of the total produced energy [2], while heat losses during transportation of such agents may exceed 25% [3]. The deterioration of heating networks, together with adoption of more stringent standards for thermal insulation, causes the need for effective heat-insulating materials.

Polymer foams have low density and, thus, superior thermal insulation properties [4-7]. Due to this, foamed polymers are widely used in civil and industrial applications [8-11]. Unfortunately, low fire safety of foamed polymers, including foamed thermosets, hinders their use in the construction industry [12, 13]. In Russian Federation, over one hundred thousand fires occur in one year, in which more than ten thousand people die [14]. A fire in a high-rise building (the height exceeds 20 floors) on average leads to the deaths of three times as many people as a fire in a building with a number of floors below nine [15]. The high cost of construction areas in large cities, being the reason for increasing the number of levels of buildings, increases the number of risk factors.

In accordance to the stated above, in the past decades there is a constant increase of interest to multifunctional construction materials: materials with low thermal conductivity and high fire safety. It is well known that foamed plastics (based both on thermoplastics and thermosets) can be efficient thermal insulators [16-19]. The main advantages of the foamed plastics are moderate cost and relatively low material consumption. But, as was already stated, the fundamental disadvantages (if compared with foamed cement concrete) are flammability and low fire safety. Because of this, development of foamed plastics with high fire safety – high limiting oxygen index (LOI), low flammability and combustibility, low smoke formation – is of great importance.

An efficient method of reducing the flammability of polymer-based materials is the use of phosphorus-containing flame retardants. To reduce the flammability of rigid polyurethane foams, microencapsulated red phosphorus [20], dimethylmethylphosphonate [21], organo-phosphorus fire retardants [22] or phosphorus-containing polyols [23] are used. To reduce the tendency of resole polyphenoplasts to smolder, it is recommended to use reactive organo-phosphorus compounds [24].

In the present work we have examined the effects of the chemical nature and the content of phosphorus-containing flame retardants on the operational properties, flammability, combustibility, smoke-generating ability and composition of pyrolysis products of several types of foamed polymers.

2 Materials and methods

Rigid polyurethane foams were synthesized on the basis of polyisocyanate and simple oxypropylated polyols Laprol-503 and Laprol-805. A mixture of nitrogen-containing polyol Lapromol-294 with dimethylethanolamine was used as catalyst for foaming and hardening. The mixture of freon-11 and water was used as foaming agents during production of polyurethane foams. Resole phenoplasts were obtained on the basis of the FRV-1A prepolymer and the VAG-3 foaming-hardening agent. Urea phenolic plastics were obtained on the basis of KF-MT resin, OP-10 surfactant, freon-11 foaming agent and hardener (25% aqueous solution of orthophosphoric acid).

The phosphorus-containing component for rigid polyurethane foams was oxyethylated tetraalkylphosphonate of pentaerythritol (phosphorus content 14.7%). To reduce the flammability of urea and resole foams, several phosphorus-containing fire retardants were used: inorganic phosphates NH4H2PO4 and (NH4)2HPO4, ammonium polyphosphate (phosphorus content not less than 31%), as well as microencapsulated polyphosphate particles with 40-150 μm diameter. The shell of microencapsulated ammonium polyphosphate particles is a copolymer of styrene and tribromophenylmaleinnimide.

Phosphate plasticizers were also used: tricresyl phosphate (phosphorus content 9.6%), diphenylisobutylphenyl phosphate (phosphorus content 8.42%), trichloropropyl phosphate (phosphorus content 9.47%), trianilidophosphate (phosphorus content 9.5%), methylphosphonic acid diamide (phosphorus content 11.6%) and poly-1,4-phenylenephenylphosphonate (phosphorus content 13.4%).

The substances containing hydroxyl (phosdiol, phosphorus content 15.5%) or methacrylate (2-phosphonoxyethyl methacrylate, phosphorus content 14.3%; phosphacrylate, phosphorus content 10.1%) groups were used as reactive organo-phosphorus compounds.

Thermal analysis of foamed polymers was carried out using a DuPONT-9900 thermoanalytical complex. Heating was carried out in air. The heating rate was 10 and 20 °C/min. The temperature of the start of intensive decomposition and the temperature of the maximum decomposition rate were taken as the criteria for thermal stability. The limiting oxygen index (LOI), characteristic temperatures (denoted as Ttl, Tv and Tsv) and the smoke production coefficient Dmax during pyrolysis and combustion were determined in accordance with RU GOST 12.1.044 and RU GOST 24632. The combustibility of phosphorus-containing foamed polymers was also determined by the ceramic tube method (RU GOST 212.044). The composition of the volatile products of pyrolysis and combustion was determined using an LKB spectrometer-colorimeter. Other operational properties were determined in accordance with the applicable local standards.

3 Results and discussion

It was found during experimental studies that increase of the phosphorus amount in rigid polyurethane foams up to 4% by weight, the LOI increases from 22 up to 29%. The flammability index decreases from 4.3 down to 0.9. The temperature of the beginning of decomposition practically does not change. The ignition and self-ignition temperatures increase by about 100 and 75 °C, respectively (Fig. 1).

A correlation was revealed between the values of limiting oxygen index and the flammability index by means of the ceramic tube testing method (Fig. 2).

As it follows from Fig. 2, rigid polyurethane foams with limiting oxygen index above 30% are slightly flammable materials. At lower limiting oxygen index values, they should be classified as moderately flammable materials. In particular, rigid polyurethane foams containing at least 2% phosphorus should be classified as such materials. At the same time, from the point of view of optimizing the complex of performance indicators of materials, the concentration of phosphorus should not exceed 3%.

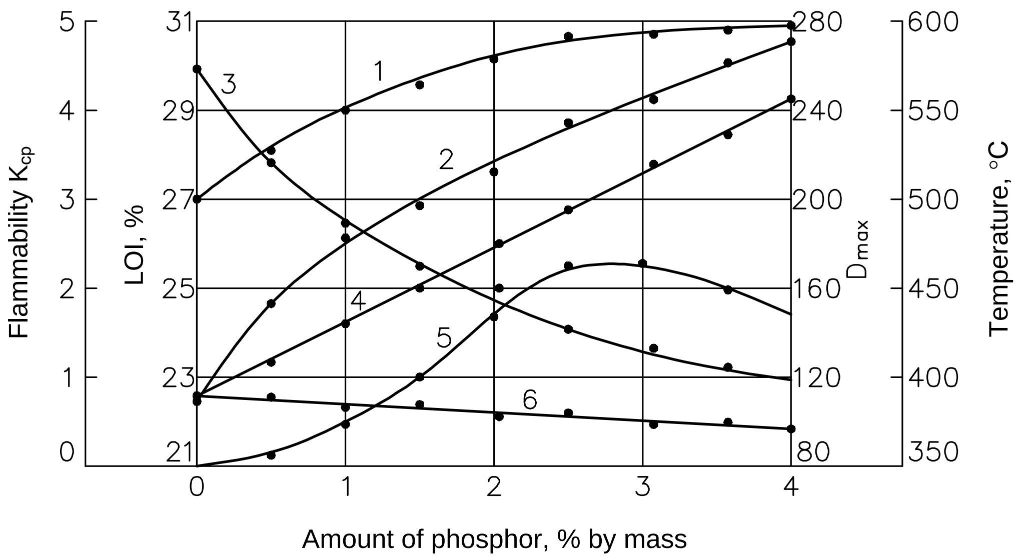

Fig 1. Dependencies of fire hazard indicators of rigid polyurethane foams on the concentration of phosphorus: 1 – self-ignition temperature; 2 – maximal smoke formation (D_{max}) in flame combustion mode; 3 – index of flammability; 4 – limiting oxygen index; 5 – ignition temperature; 6 – maximal smoke formation (D_{max}) in pyrolysis mode.

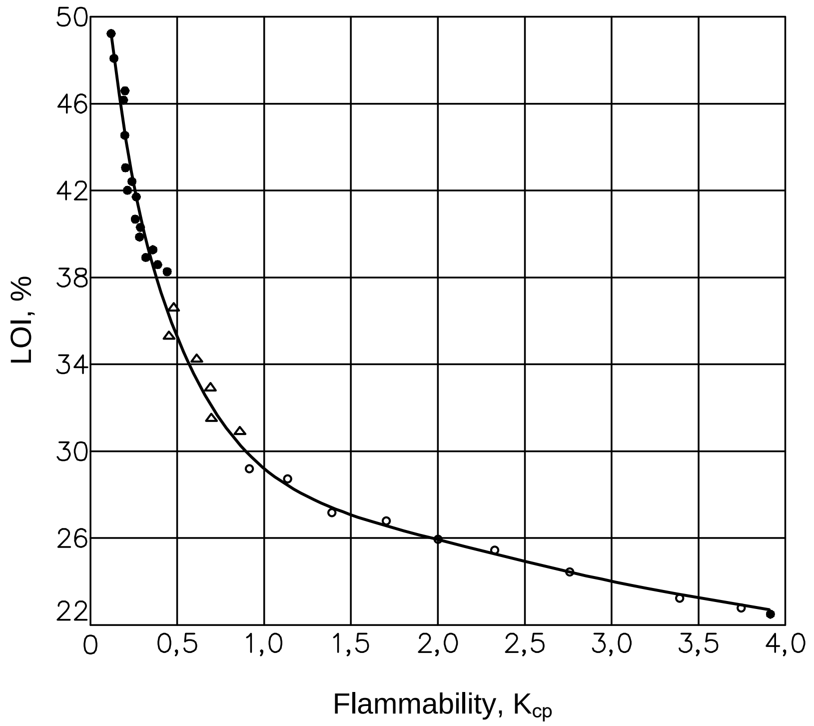

Fig 2. Correlation between limiting oxygen index and flammability index of polyurethane foams.

Analysis of the spectra of combustion products of rigid phosphorus-containing polyurethane foams showed that an increase in the phosphorus content leads to a decrease in the concentration of carbon dioxide and an increase in the content of water vapor in the combustion products. The compositions of the volatile products of pyrolysis of polyurethane foams in the temperature range from 300 to 800 °C are weakly dependent on the phosphorus content and are mainly determined by the pyrolysis temperature.

The thermal stability of urea foams weakly depends on the method of synthesis of urea oligomers, the chemical nature of the blowing agent, and the method for producing foams. In particular, the temperature of the beginning of decomposition of all such foams is about 180 °C, and the temperature of the maximum decomposition rate is about 260 °C. The values of the limiting oxygen concentration during flame propagation are also close (near 31%). The use of isopentane as a blowing agent for urea foams cannot be recommended, because it leads to a decrease of the limiting oxygen index down to 30%. A decrease of the pore volume of urea foams leads to a natural decrease in flammability. An increase in density from 45 to 154 kg/m3 leads to an increase of the limiting oxygen index up to 41%.

To obtain urea foams with reduced toxicity of pyrolysis and combustion products, it is advisable to use diammonium phosphate. With an increase of concentration of diammonium phosphate the emission of carbon monoxide and carbon dioxide decreases. The weight loss of the samples is practically independent of the chemical nature of the fire retardants and is about 75% at a temperature of 450 °C.

The combustibility of urea foams naturally decreases with an increase of the content of phosphorus-containing fire retardants up to 3%. The limiting oxygen index increases from 34 up to 40%, the flammability index (ceramic tube testing method) decreases from 1.2 down to 0.3%.

Ignition and self-ignition temperatures of urea foams increase with increasing of phosphorus content (Fig. 3).

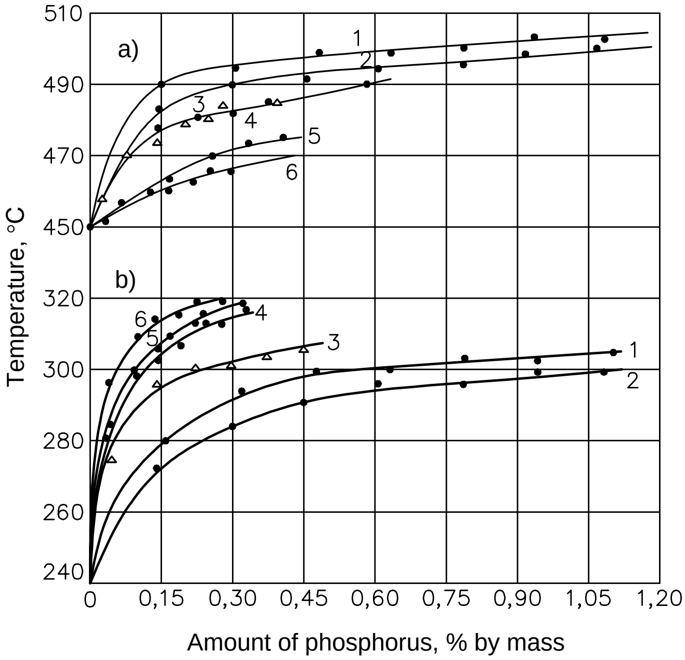

Fig. 3. Dependencies between temperatures of self-ignition (a) and ignition (b) of urea foams, amount of phosphorus and type of fire retardant (1 – ammonium polyphosphate; 2 – microencapsulated ammonium polyphosphate; 3 – Fostetrol-1; 4 – trianilidophosphate; 6 – diphenyl(isobutyl-phenyl)phosphate).

During testing, an increase in the heating rate leads to an increase in the temperature of the start of decomposition and the temperature of the maximum decomposition rate of urea foams.

To obtain urea foams with high operational properties, the concentration of phosphorus-containing fire retardants should not exceed 2.0% (amount of phosphorus is about 0.3%). At a higher concentration of fire retardants, the induction period and the duration of foaming increase. Achieving a low concentration of fire retardants and, at the same time, a relatively high concentration of phosphorus is possible when using an aqueous solution of phosphoric acid as a curing agent.

It was revealed that additive organo-phosphorus compounds can not be classified as efficient fire retardants of foamed resole polymers. In particular, polyphenylenephenylphosphonate plays rather the role of a non-combustible filler. Nevertheless, the use of additive organo-phosphorus compounds allows the oxygen index to be increased up to 49%. The effect of the phosphorus content in resole foams on the limiting oxygen index is illustrated by Fig. 4.

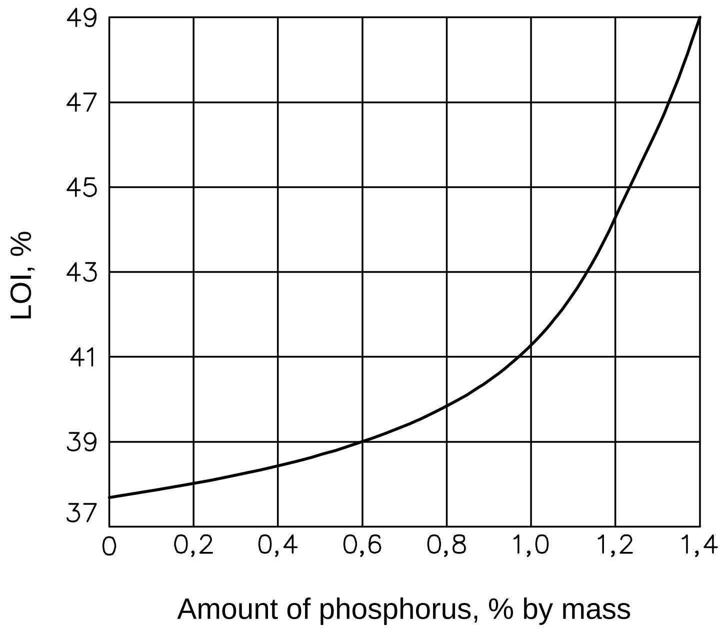

Fig 4. The dependency between phosphorus content and limiting oxygen index of resole foams.

As it follows from Fig. 4, high amount of phosphorus (significantly higher than 0.3%) and high LOI of resole foams can only be achieved when using fire retardants with high phosphorus content. It should be noted that for resole foamed plastics, as well as for polyurethane foams, there is a correlation between the limiting oxygen index and the flammability index.

It was also shown that foamed phenolic plastics with high operational properties can be produced with organo-phosphorus compounds which interact with phenol-formaldehyde oligomers during their curing or form interpenetrating spatial networks with such oligomers. Organo-phosphorus compounds containing methacrylate or hydroxyl groups combine well with most phenoplasts, only slightly increasing the foam rise time and the foaming duration. This increases the strength of foams and the quality of thermal insulation products based on them.

The suppression of the smoldering process (Fig. 5) of phenoplasts with organo-phosphorus compounds occurs due to a sharp decrease in heat release as a result of a decrease in the rate and heat of the oxidation reaction of the carbonized residue.

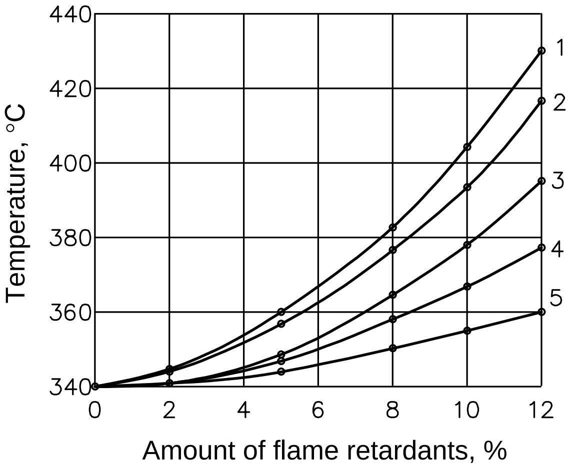

Fig 5. The dependencies between amount of flame retardants and smoldering temperature of resole foams (types of flame retardants: 1 – Phosdiol; 2 – Fostetrol; 3 – 2-phosphonoxyethylenetet acrylate; 4 – sulfacrylate; 5 – trianilidophosphate).

When exposed to flame, there is a constant transformation of phosphorus-containing fire retardants into the structure of polyphosphoric acids. The efficiency of organo-phosphorus compounds is due to a change in the nature of pyrolysis of phenol-formaldehyde polymers. At the initial stage, a viscous-flowing melt is formed and foamed. At the next stage, the remainder passes into a solid non-volatile state.

4 Summary and conclusion

In the present work the dependences between fire hazard indicators foamed polymers (rigid polyurethane foams, resole and urea foams) and the concentration of various phosphorus-containing fire retardants have been experimentally investigated. The optimal concentrations of phosphorus have been determined, which make it possible to obtain fire-safe heat-insulating materials with high operational properties (Table 1).

Table 1. Some operational properties of the developed foams

Property	Resole foams	Polyurethane foams	Urea foams
Density, kg/m^3	65...75	43...50	130...150
Compressive strength, kPa	100...120	260...280	700...1300
Flexural strength, kPa	100...110	210...230	800...1400
Temperature of start of decomposition, °C	290...295	182...185	170...175
Temperature of ignition, °C	540...560	460...470	295...310
Temperature of self-ignition, °C	>600	580...590	465...500
LOI, %	44...45	28...29	40...42
Heat conduction, mW/(m·K)	35...38	30...32	41...45

Thus, by means of admixture of organo-phosphorus compounds it is possible to develop rigid polyurethane foams, urea and resole foams with low fire hazard and high operational properties.

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