Synergetic flame retardant effect of bio-flame retardant based on oxidized wood in polyester’s compositions

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Abstract. Synthesized bio-flame retardants from plant materials. A comparative analysis of the flammability indices of polyester resin samples containing complex double flame retardants and single flame retardants of bioantipyrene, aluminum hydroxide and ammonium polyphosphate showed a non-additive improvement in flame retardant compositions consisting of double flame retardant compositions.

Unsaturated polyester resins are polymer mixtures containing unsaturated groups and styrene, which acts as a cross-linking agent in the process of radical polymerization [1]. Unsaturated polyester resins can take two forms, depending on the polyester part: orthophthalic or isophthalic. Most unsaturated polyester resin formulations cure at room temperature. However, catalyst, accelerators, and temperature can be used to accelerate the reaction [2]. Additives, including flame retardants, can be easily incorporated into unsaturated polyesters at the processing stage. Good manufacturability, good mechanical properties, water and corrosion resistance and relatively low cost make them ideal for use (trains and ships) [3-5]. Unsaturated polyesters are highly flammable and emit large amounts of smoke during combustion [6].

The addition of halogens is very effective in reducing flammability and, despite environmental problems, it is still the main method by which low flammability of materials is achieved. Halogenated polyesters are effective only if they themselves are sources of ignition, otherwise they will burn together with other combustible components with the release of heat and toxic products. Also, halogen-containing resins have slightly worse mechanical properties compared to conventional polyesters [7].

The main reason for the high combustibility and increased heat release of polyester composites is that during their pyrolysis, 95 - 98% of combustible volatile substances are formed, and coke formation is practically absent [7].

The process of thermal decomposition of all unsaturated polyesters leads to the formation of various low molecular weight volatile substances, including CO, CO₂, methane, ethylene, propylene, butadiene, naphthalene, benzene, toluene, etc. [8 -10].

Significant disadvantages of polyesters under combustion conditions are their increased smoke formation due to the presence of styrene fragments in the polymer chain, as well as the formation of burning drops of liquid pyrolysis products. The accumulation effect can be reduced by using composite materials with a high content of inorganic inert flame retardants [11].

As a rule, aluminum hydroxide with the addition of phosphorus is used as flame retardant additives. It should be noted that magnesium hydroxide is not recommended for use in polyesters, since it accelerates their destruction. The combined use of aluminum hydroxide with ammonium polyphosphate is possible: in this case they form a composition with intumescent properties [12].
synergistic effect of reducing the combustibility of polymer composites with the combined use of ammonium polyphosphate and graphite was also previously shown [13]. The use of melamine and its salts as flame retardants is less effective compared to ammonium polyphosphate [14].

Some flame retardants, such as hydrated mineral fillers, nanoclay and other aluminosilicates are found in nature, and have low toxicity. Other inorganic flame retardants, such as ammonium polyphosphate, also have low toxicity, but decompose in the environment over time.

However, a global problem for many representatives of synthetic halogen- and phosphorus-containing flame retardants lies in their high toxicity and the potential for the formation of carcinogenic compounds in the process of destruction and combustion. Halogen-containing flame retardants, inhibiting the combustion process in the gas phase and reducing heat generation, contribute to the formation of products of incomplete combustion. In most cases, death from a fire occurs as a result of inhalation of toxic products of pyrolysis and combustion of materials, while halogen-containing flame retardants sharply increase the toxicity of combustion products.

Today, one of the solutions to the toxicity of bio-flame retardants (BFR) is the use of intumescent coke-forming systems [15, 16]. In particular, much attention is paid to developments in the field of creating modern environmentally friendly intumescent fire retardants of natural origin in the world.

In order to prepare a fire-retardant solution, 20 liters of hot water, 25 g of CuSO₄ · 5H₂O and 2.8 kg of coniferous wood flour with a moisture content of about 5.5% are introduced into a steel sealed reactor with a volume of 0.04 m³ heated to 60 °C. The mixture was stirred with a mechanical stirrer for 2 minutes at a stirring speed of 50 rpm, then 1.3 kg of NaOH was added. In addition, the stirring speed increases to 140 rpm, the reactor is sealed, and gaseous oxygen is supplied from above to the reactor at a rate of 0.2 l/min. During the reaction, a constant temperature of 60 °C is maintained. The oxygen pressure in the reactor during the entire oxidation process is maintained at 3 atm. The time of completion of the oxidation reaction is determined by the concentration of free alkali by titration with 0.1 N HCl in the solution to 0.5 - 0.8 M. The reaction mixture was filtered in order to separate from the solid impurities, the filtrate was dried at 60-70 °C. Finally the dried light brown product was crushed to the particle size less than 80 microns.

All the samples with BFR were prepared with the use of pristine polyester resin (RPE) with all components without flame retardant in accordance with the standard formulation using hardeners, a release agent and a UV stabilizer.

Further, complex compositions were prepared on the basis of the obtained mixtures (RPE) and various flame retardants, including flame retardant BFR, Al(OH)₃ and ammonium polyphosphate - (NH₄PO₃)ₙ, where (n > 1000):

1. RPE - 100 mass parts (sample №1);
2. RPE - 100 mass parts / flame retardant BFR - 30 mass parts. (sample №2);
3. RPE - 100 mass parts / Al(OH)₃ - 30 mass parts. (sample №3);
4. RPE - 100 mass parts / ammonium polyphosphate - 30 mass parts. (sample №4);
5. RPE - 100 mass parts / flame retardant BFR - 20 mass parts. + Al(OH)₃ - 10 mass parts. (sample №5);
6. RPE - 100 mass parts / flame retardant BFR - 10 mass parts. + Al(OH)₃ - 20 mass parts. (sample №6);
7. RPE - 100 mass parts / flame retardant BFR - 20 mass parts. + ammonium polyphosphate 10 mass parts. (sample №7);
8. RPE - 100 mass parts / flame retardant BFR - 10 mass parts. + ammonium polyphosphate - 20 mass parts. (sample №8).

The resulting mixture was stirred with a disk stirrer for 10 minutes at a speed of 800 rpm. Resulting composition was cured at 140-150 °C for 1 hour.

A comparative study of the combustibility characteristics of polyester compositions containing BFR flame retardant and aluminum trihydrate was the main task that was solved at the first stage. In this case, it was necessary to determine the optimal concentration of the introduced flame retardant A (as compared with Al(OH)₃) to create a low flammability polyester composition.
The flammability of samples of polyester resin compositions containing BFR flame retardant and aluminum trihydrate was studied using a device we developed — a mass calorimeter that allows one to determine the mass loss rate during burning of samples [RF Patent “Device for testing combustibility materials” No. 119115]. The principle of operation of the mass calorimeter is to determine the main parameters of the heat balance of the combustion process in an average fire, namely: the rate of heat generation and the rate of weight loss (ASTM 1354-92, ISO / DIS 13927).

In the general form, the scheme of heat balance for the cone (mass) calorimetry testing of samples is given in Figure 1.

**Figure 1.** Heat balance scheme in cone calorimeter tests; \( \delta \) is the sample thickness.

The total heat flux \( Q_{tot} \) is composed of an incident heat flux from an external heater \( Q_{ex} \), a heat flux from the flame on the surface of the material \( Q_{fl} \), and heat losses due to convection \( Q_{conv} \) and radiation to the surroundings \( Q_{rad} \).

A phenomenological equation relating the mass loss rate to the net heat flux during combustion may be represented by

\[
\cdot m = \frac{Q_{tot}}{L_g} + \frac{Q_{fl} - (Q_{rad} + Q_{conv})}{L_g}
\]  

(1)

where \( L_g \) (kJ/g) is the heat of gasification related to the total heat flux on the surface. In practice, \( L_g \) is determined from the slope of the plot of the mass loss rate as a linear function of external heat flux.

The basic equation relating the mass loss rate to the heat release rate during combustion is as follows:

\[
\dot{Q}_{tot} (kW/m^2) = \chi \cdot \Delta H_{comb} \cdot \cdot m
\]  

(2)

Here, \( \chi \) is the combustion efficiency, \( \Delta H_{comb} \) is the heat of complete combustion, and \( \cdot m \) is the rate of mass loss per unit surface.

If \( \Delta H_{comb} \) is a constant value for given materials, i.e. since there are no gas-phase inhibition processes in the flame, the heat release rate linearly depends on the mass loss rate. In this case, the coefficient \( \chi \) for the linear equation characterizing the combustion efficiency or the completeness of
combustion directly depends on the amount and structure of the carbonaceous residue. It is known that the fire protection mechanism of materials containing intumescent and coke-forming flame retardants mainly describes reactions in the solid phase, while the effective values of the calorific value are independent of the introduced flame retardant. Therefore, the main indicator of combustibility - the rate of heat release in this case is directly proportional to the rate of mass loss \((\frac{dm}{dt})\). Thus, the maximum mass loss rate \((\frac{dm}{dt})\) characterizes the combustibility of the material.

Under test conditions, samples placed on an electronic balance were subjected to a constant heat flux of 20 kW/m², providing a surface temperature of about 500 °C, from an infrared heater. After a certain time (induction period), ignition of the samples occurred. Data on the change in the mass of the sample at equal intervals (2 seconds) were transmitted to a computer. All studied samples had the same surface area (disks with a diameter of 15 mm) and a mass of 0.750 ± 0.200 g. By differentiating the time dependence of the mass loss on temperature, we determined the dependence of the mass loss rate on temperature \((\frac{dm}{dt})\). From the obtained data, the period of ignition induction was further determined as the time of the start of a noticeable deviation, the mass loss rate \(\frac{dm}{dt}\) proportional to the maximum heat release rate, and also the maximum mass loss rate satisfying the condition \((\frac{d^2m}{dt^2} = 0)\) when exposed to an external heat flux 20 kW/m².

Flammability tests were conducted for samples of a polyester resin containing BFR flame retardant, as well as Al(OH)₃ flame retardant and ammonium polyphosphate.

![Figure 2](image_url)

**Figure 2.** General diagram of the values of the maximum mass loss rate of samples of polyester compositions under conditions of combustion at an external heat flux of 20 kW/m².
Figure 3. A general diagram of the values of the selfignition induction period of samples of polyester compositions under conditions of combustion at an external heat flux of $20 \text{ kW/m}^2$.

Comparison of the maximum mass loss rate of polyester compositions containing a flame retardant additive BFR at a concentration of 30 mass. p (sample №. 2) with similar compositions containing aluminum hydroxide and ammonium polyphosphate (samples № 3 and №. 4, respectively) shows a higher efficiency of the flame retardant additive BFR compared with aluminum hydroxide and ammonium polyphosphate in terms of the maximum mass loss rate.

The results of the flammability indicators of the compositions of the polyester resin containing a double flame retardant additive: a flame retardant additive BFR, aluminum trihydrate and ammonium polyphosphate (№ 5-8) clearly illustrate the synergism of the joint action of flame retardants.

A comparative analysis of the flammability indices of polyester resin samples containing complex double flame retardants and single flame retardants of aluminum hydroxide and ammonium polyphosphate showed a non-additive improvement in flame retardant compositions consisting of double flame retardant compositions. Moreover, the flammability indices of all flame retardant additives individually are worse than for binary flame retardant compositions, which is evidence of the synergistic effect manifested in systems containing flame retardant additives BFR, aluminum hydroxide or ammonium polyphosphate.

The introduction of BFR can significantly increase the fire retardant effect of traditional flame retardants, such as aluminum hydroxide and ammonium polyphosphate due to the combined thermochemical transformations during high-temperature pyrolysis and combustion.

This work was carried out with financial support of the Ministry of Education and Science of the Russian Federation on government contract № 05.607.21.0304 (RFMEFI60719X0304) "Development of effective ways of chemical inhibition of homogeneous and heterogeneous processes of burning and creation of the demonstration sample of technogenic waste detonation converter" under a special
federal programme "Research and Development in the Priority Directions of Development of a Scientific and Technological Complex of Russia for 2014-2020".

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