RESEARCH OF THE OXYGEN INDEX OF FIRE-RESISTANT POLYMER MATERIALS OBTAINED ON THE BASIS OF OLIGOMERIC BINDERS CONTAINING NITROGEN, PHOSPHORUS

[1]Sadikov R.M., [2]Nurkulov F.N., [3]Djalilov A.T.
[1,2,3]Tashkent Scientific Research Institute of Chemical Technology
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Abstract. *In this article, a lot of attention is paid to obtaining fire-resistant aluminum composite panels based on fire retardant containing phosphorus and nitrogen. In addition, changes in physical-mechanical properties of refractory polymer materials based on different standard requirements were studied.*
Keywords: *fire-resistant compositions, oligomer flame retardant, aluminum composite panels, composite materials, modifiers, oxygen index.*

Introduction. Synthetic polymer materials, particularly polyolefins, are highly flammable materials. Knowing that polyolefins (PO) are large-ton synthetic polymers widely used in all sectors of the economy, it is necessary to reduce their flammability because they have the lowest fire resistance and oxygen index (KI) of 17.0 - 22.0%. [1, 2, 3]. Combustibility of polymeric materials depends on the nature, chemical composition and structure of the materials. Usually, the initial stages of the combustion process are determined by the formation of weak bonds, the oxidation of hydrocarbon fragments, the formation of carbon-carbon and carbon-element bonds (without heteroatoms in the chemical structure), which later lead to the formation of gaseous and condensable products. From the point of view of ignition and combustion, any polymer material contains "fuel", that is, fragments that can be thermally decomposed and thermally oxidized.

Table -1

Flammability of Composite Polymer Matrix

Polymer	Fire temperature °C	LOI (%)	Thermal degradation temperature	The total heat of combustion is 50 current (kJ/g)	The highest rate of heat release is 50 current (kW/m^2)	Smoke return 50 flow (m^2/kg)
Polyethylene	370	18	399	37	1130	362
Polypropylene	330	18	354	44	1300	621
Nylon-6	430	25	424	30	1272	160
Polycarbonate	500	25	476	31	-	-
poly(styrene)	319	18	356	28	407	546
Poly (acrylonitrile)	480	27	320	28	343	140
Epoxy resins	427	19	427	25	755	866
Unsaturated Polyester	330	20	380	23	985	801

In this case, the probability of reaching the limit of self-extinction increases with the formation of bonds under the influence of heat, oxidation, and heat stress with a high level of dissociation energy. It is noteworthy that for PO, the carbon-oxygen bonds formed during the thermal oxidation and combustion process exceed the original carbon-carbon bonds. [2, 3, 4, 5].

Combustion of any material requires three components: heat, oxygen, and combustible material or fuel. This mechanism is known as the condensed phase mechanism. In this case, during combustion, the chemicals of the fire retardant release more non-combustible gases, which leads to a decrease in the effective concentration of oxygen in the fire zone, thereby acting as a flame retardant agent. [6, 7, 8, 9].

The fire resistance of a composite material can be improved in two ways. The first is by increasing the fire resistance of composite components. The second is with a protective fireproof coating around the core composites. There are various ways to improve the fire resistance of composite materials by changing the components and using protective coating [10, 11].

Methods and materials. The performance characteristic of plastic, which limits its use for a number of tasks, is flammability. And one of the characteristics of fire resistance, and therefore fire safety of polymer materials, is the oxygen index. CI reflects the minimum oxygen content at which combustion of the material can be maintained.

Flammability is expressed in the ability of a material to ignite, maintain and spread combustion. This process depends on different quantities: ignition temperature, auto-ignition temperature, burnout rate, fire spread rate, heat release intensity, toxicity. This process is also influenced by factors such as atmospheric composition, air density, and oxygen index. So, combustion is a complex characteristic that significantly hinders the widespread adoption of plastics in various segments of industries.

Oxygen index (OI) - is the minimum volume percentage of oxygen in an oxygen-nitrogen mixture at which candle-like combustion of materials is possible under special test conditions.

The CI value is used in the development of polymer compositions of reduced flammability and control of the flammability of polymer materials. The experimental method for determining CI, according to ГОСТ 12.1.044-89, is to find the minimum oxygen concentration in the flow of an oxygen-nitrogen mixture at which spontaneous combustion of a vertically located sample ignited from above is observed. The oxygen index (in%) is calculated using the formula:

$$OI = V_к/(V_к+V_a).\ 100,$$

where Vk and Va - are the volumetric flow rates of oxygen and nitrogen, respectively (l/min or cm^3/s). The arithmetic mean of at least three determinations is taken as the test result. In the air atmosphere the percentage of oxygen is 21%. Thus, if the CI value of a material is below 21%, this material will support combustion in air.

Results and discussion. The simplest way to change the thermal balance and increase heat loss is by gluing a polymer to the surface of a heat-conducting, for example metal, product. If the product itself is quite massive and the thickness of the polymer is not too large, then the flammability of the structure can be significantly lower than the polymer itself. The thinner the polymer layer, the greater the heat loss through the polymer into the substrate and the more severe conditions spontaneous combustion can occur.

The introduction of inert fillers into the polymer is another way to reduce the flammability of a polymer material. Inert fillers are understood as those that do not have a significant effect on the composition and quantity of polymer pyrolysis products in the gas phase and the amount of coke residue under combustion conditions. They can be divided into two groups:

1) mineral fillers, stable up to a temperature of 1000°C - metal oxides, calcium and lithium fluorides, silicates, carbon black, inorganic glass, powdered metals, etc;

2) substances that decompose at temperatures below 400 – 500°C with the absorption of heat and usually with the release of carbon dioxide and/or water vapor, ammonia - hydroxides, metal bicarbonates, ammonium phosphates, etc. [12].

Additional heat when introducing fillers of the first group is spent only on heating the filler from the initial temperature to the temperature of the polymer surface. However, as it turns out, in the heat balance the contribution of such heating is small and the change in the oxygen index with the introduction of a reasonable amount of filler is small. A greater effect can be obtained by introducing a filler that decomposes with heat absorption. A classic example of such a filler is aluminum hydroxide $Al(OH)_3$, from which water is separated. In this case, heat is spent both on heating the filler and on decomposing the filler and heating the resulting water to the flame temperature, and a noticeable increase in the oxygen index is observed at an $Al(OH)_3$ content of about 55 - 65 wt. %. In this case, the reduction in flammability significantly depends on the ratio of heat loss due to the decomposition of the filler and all other heat losses from the flame, which are always higher, the greater the total heat of combustion of the polymer. Therefore, the introduction of 60% $Al(OH)_3$ into polyethylene does not lead to a significant increase in the oxygen index (CI increases from 17.5 to 25 - 26), while the CI of polyformaldehyde, which has a significantly lower calorific value, increases from 15. 3 to ~40 [13].

Another way to increase heat loss and reduce flame temperature is to increase infrared radiation. If the hottest region of the flame does not contain solid particles, then near the combustion limit (Tm = 1000 – 1100°C) radiation losses are negligible. However, when certain compounds are introduced into the polymer, for example bromine-containing and phosphorus-containing compounds, antimony trioxide along with halocarbons, the flame luminosity increases significantly due to the formation of soot and the appearance of other solid particles. It is interesting that in this case the radiation flux from the flame and onto the polymer increases. Therefore, although the combustion limits shift towards higher oxygen index, combustion rates above the limit increase with the introduction of such compounds. In other words, these compounds, on the one hand, inhibit combustion (shift the limits of combustion), and on the other hand, they can promote it, increasing the rate of burnout, or the spread of flame over the surface of the polymer. The rate of the chemical oxidation reaction in the gas phase can also be reduced by chemical inhibition. This method is especially effective when the proportion of the chain process in gas flame reactions is sufficiently large [13, 14].

New fire safety problems also arise in connection with the accelerated construction of residential, industrial and public buildings. The likelihood of a fire can be reduced by using materials that are difficult to ignite in buildings, protecting them with special fire-retardant compounds.

New multifunctional organometallic fire retardants were synthesized based on the interaction products of nitrogen, phosphorus, and metal-containing compounds, while the properties of fire-retardant grades FPM-2 (highly filled fire-retardant polymer material) were studied. The resulting composition was studied for its oxygen index based on organometallic fire retardant and recycled polyethylene. The amount of fire retardant in the composition is 10-30% by weight of the polymer.

The additive and granules of the original polymer are mixed and loaded into the hopper of the injection molding machine. Extrusion is carried out under conditions that do not differ from the processing conditions of the corresponding industrial grades of the original polymers. The table shows the flammability characteristics of polymer materials using the proposed additive obtained grade FPM-2. From the data presented in the table it follows that the introduction of the proposed additive significantly increases the oxygen index of polymer compositions, which is a fundamental criterion for their inflammability. From the data presented it also follows that the greatest effect is achieved when using the additive on thermoplastics such as polyethylene. The parameters of the oxygen index according to ГОСТ-12.1.044-84 also testify in favor of the proposed additive and achieve the greatest value when using the latter on thermoplastics such as polyethylene.

Table 2

Effect of flame retardant concentration on the oxygen index.
ГОСТ-12.1.044-84

Fire retardant grades FPM-2	Oxygen index. %
-	recycled polyethylene
0	19,5
5	23,0
10	28,3
15	31,5
20	36,4
25	38,7
30	40,3

The additive production process can be carried out at chemical industry enterprises producing oligomeric flame retardants using standard chemical equipment. Research on the oxygen index of the polyethylene composition is CI 23-40.3%.

Thus, the effectiveness of using composite inorganic fillers with phosphorus-, nitrogen-containing oligomeric fire retardants as fire retardants of polyolefin building materials for highly filled polyethylenes has been proven.

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