Copolyesters based on 3,5-dibromo-4-hydroxybenzoic acid chloranhydride

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Abstract. Modified copolyesters using 3,5-dibromo-4-hydroxybenzoic acid chloride have been synthesized by the method of low-temperature polycondensation (acceptor-catalytic polycondensation). The main laws governing the synthesis of copolyesters have been studied. It was found that the presence of bromine atoms reduces the reactivity of the hydroxyl group due to the steric effect, as well as due to the possible formation of a weak hydrogen bond between the bromine and hydrogen atoms of the hydroxyl group. The main physical and mechanical characteristics of the synthesized copolyesters have been investigated. Copolyesters are heat- and fire-resistant high-strength polymers that can be used in various industries as non-combustible heat-resistant structural polymer materials.

1. Introduction
The creation of heat-resistant structural polymer materials that can withstand high temperature operating conditions and have good fire resistance is one of the priority areas of world polymer chemistry. Expansion of the range and creation of new materials with high performance characteristics (specific strength indicators, chemical resistance, corrosion resistance, fire resistance, etc.) is an important and urgent task. All these requirements are met by polymers based on 4-hydroxybenzoic acid.

The development of methods for obtaining polymeric materials with a new set of properties is carried out in various directions, one of which is the modification of known polymers, which makes it possible to change the initial properties of polymers and thereby obtain new materials [1-5].

This work is an integral part of the research carried out under the project "Fundamental problems of creating composite materials for the aerospace industry".

The experience gained to date in the operation of polymer composites in critical structures of aviation and space technology has shown that their use instead of metal alloys has reduced the mass of structures to 30-50%, increased the service life by 2-5 times, reduced the labor intensity of manufacturing by 20-40% and material consumption up to 50%, along with giving the construction materials a number of special properties, i.e. making them multifunctional [6-11].

The operating conditions of aviation equipment determine extremely stringent requirements for materials, which must ensure: structural strength with a minimum specific weight, dimensions and fuel consumption; reliability and long service life when exposed to variable and significant power loads, with alternating high and low operating temperatures, climatic factors, corpuscular, electromagnetic X-rays, etc. [12-18].

To create materials that meet these requirements, it was of interest to use a brominated derivative of p-hydroxybenzoic acid as one of the monomers in the synthesis of copolyesters by acceptor-catalytic polycondensation.
2. Experimental
The synthesis of terephthaloyl-di- (4-hydroxybenzoic) acid was carried out according to the following scheme: 0.1 mol of terephthalic acid dichloride, 200 ml of carbon tetrachloride was loaded into a three-necked round-bottom flask with a capacity of 1 l, equipped with a mechanical stirrer, at room temperature. Then, with vigorous stirring, the prepared solution was added dropwise, consisting of 0.3 mol of 4-hydroxybenzoic acid and 0.3 mol of sodium bicarbonate in 700 ml of distilled water. Stirring of the reaction mixture was carried out for 2-2.5 hours, the formed precipitate was filtered, washed with an aqueous solution of sodium bicarbonate, distilled water and transferred to a glass, where it was dispersed in 1 L of 1 N HCl solution. After that, the resulting substance was filtered, washed several times with distilled water and dried in a vacuum oven for 6 hours. Thus, the formation of terephthaloyl-di- (4-hydroxybenzoic) acid of the formula C22H14O8 is confirmed by the data of elemental analysis and IR spectroscopy.

Polymer films were obtained by pouring a 5% polymer solution in chloroform onto a smooth cellophane substrate, followed by slow evaporation of the solvent at room temperature. The resulting films were dried in vacuum with a gradual increase in temperature from room temperature to 50 °C for 3-6 hours. Then the polymer films were kept in vacuum at 80-1000 °C to constant weight.

Determination of the reduced viscosity was carried out in an Oswald viscometer with a hanging level, at a temperature of T = 25 °C for a concentration of 0.5 g/dl. The capillary diameter of the viscometer was selected so that the flow time of the pure solvent was within the range of 100-200 seconds in order to avoid corrections for kinematic viscosity.

The study of the molecular weight distribution (polydispersity) of polymers was carried out by the method of turbidimetric titration, carried out on a FEK-56M device.

IR spectral studies were carried out on a Perkin Elmer SPECTRUM TWO IR spectrometer using powdered samples in the range from 4000 to 450 cm⁻¹.

Thermogravimetric analysis was carried out in the range from 30 to 750 °C using a Perkin Elmer TGA 4000 instrument with a heating rate of 5 °C/min, a sample weight of 25 mg, the medium was air.

Phase transitions were studied on a Perkin Elmer DSC 4000 differential scanning calorimeter (DSC) at a heating rate of 5 °C/min in air.

Flammability by the oxygen index (OI) method was determined according to GOST 12.1.044-89 on specimens in the form of a bar 80-120 mm long, 10 ± 0.5 mm wide and 3-4 mm thick.

3. Results and discussions
The use of plastic products in many areas of technology places increased demands on them, especially with regard to their resistance to open fire and high temperatures. Therefore, an urgent task is to create fire and heat resistant polymers, including those based on aromatic polyesters. The use of halogen-containing chemically active combustion inhibitors introduced in the process of polymer synthesis, methods of imparting a fire-resistant method is the most effective way to reduce the combustibility of polymer materials. Aromatic hydroxy compounds, to which 4-hydroxybenzoic acid belongs, are promising in this respect. 4-hydroxybenzoic acid and its derivatives are widely used in the synthesis of heat-resistant polymers; however, the possibility of using halogen-substituted 4-oxenbenzoic acid as a flame-retardant additive in the synthesis of aromatic polyesters has hardly been studied.

The reaction of synthesis of copolyarylates by the method of acceptor-catalytic polycondensation according to the scheme:
The regularities of acceptor-catalytic polycondensation in the synthesis of copolyesters based on acid chloride, 3,5-dibromo-4-hydroxybenzoic acid, and 3,3-bis-(4-hydroxyphenyl) phthalide have been studied.

As a result of the studies carried out, the optimal conditions for achieving modified copolyesters: the solvent is dichloroethane, the reaction temperature is 200°C, the synthesis time is 2 hours, the solution is 0.5 mol/L, the amount of triethylamine is equimolar to various hydroxyl groups.

The reactivity of 3,5-dibromo-4-hydroxybenzoic acid chloride is determined by electron-acceptor substituents located in the o-position with respect to the hydroxyl group. The presence of elements of the bromine group reduces the reactivity of the hydroxyl group due to the steric effect, as well as due to the possible formation of a weak hydrogen bond between the bromine atoms and the hydroxyl group. This, for a more complete use in the reaction of a modifying additive - 3,5-dibromo-4-hydroxybenzoic acid chloride, polycondensation in two stages, each of which lasted 1 hour.

Taking into account the regularities found, polyesters of various compositions were synthesized, which are modified polyesters based on 3,3-bis-(4-hydroxyphenyl)phthalide, 1 to 20 mol.% Residues of modifying comonomer 3,5-dibromo-4-hydroxybenzoic acid from the total amount 3,3-bis-(4-hydroxyphenyl) phthalide.

The yield and reduced viscosity of halogen-containing copolyesters with a modifier content of more than 10 mol% decreases with increasing concentration of 3,5-dibromo-4-hydroxybenzoic acid chloride in the reaction mixture. The reason for this may be the reduced solubility of the modifier, and, obviously, the steric effect caused by bulky bromine atoms. Although the reactivity of the modifier is inferior to the initial reagents, it is sufficient to achieve high molecular weight polymers under the conditions of acceptor-catalytic polyesterification.

In order to determine the performance characteristics of modified polyesters, some of their physicochemical properties have been studied.

A study of the thermomechanical properties of polyesters showed that the temperature of the modifier body from 0 to 10 mol.% Varies from 250 to 273°C. A further increase in the modifier content leads to a significant drop in this indicator of polymers, which is probably associated with a noticeable drop in the molecular weight of the latter.

Studies have shown that the presence of 3,5-dibromo-4-hydroxybenzoic acid chloride units increased strength characteristics of copolymers based on 3,3-bis-(4-hydroxyphenyl)phthalide (table).
Table 1. Some properties of modified polyesters

| Modifier content, mol% | Breaking strength σ, MPa | Breaking elongation ε, % | Elastic modulus E, GPa | Heat resistance, °C | Oxygen index, % |
|------------------------|--------------------------|--------------------------|-----------------------|---------------------|----------------|
| 1                      | 85                       | 10,5                     | 5,7                   | 405                 | 31,5           |
| 5                      | 100                      | 13,5                     | 6,1                   | 400                 | 37,0           |
| 10                     | 106                      | 12,5                     | 8,6                   | 425                 | 45,5           |
| 20                     | 90                       | 5,0                      | 5,2                   | 370                 | 47,5           |

Considering the results of testing the materials under study, it should be emphasized that, from the synthesized polymers, it was possible to make strong, optically transparent films with high mechanical properties and good thermal stability. When introduced up to a certain limit (up to 10 mol%), the effect is demonstrated by a noticeable increase in the material (an increase in the elastic modulus and plasticity limit) when introduced up to a certain limit (up to 10 mol%).

The maximum values of the breaking stress are characteristic of polyesters with modifier elements of 5 and 10 mol%. A slight increase in strength with the introduction of a modifying agent is probably due to the ordering of the structure of macromolecules due to intermolecular interaction caused by polar bromine atoms. A decrease in the value of the relative elongation upon deformation for samples, more than 10 mol.% Of the Modifier is due to the fact that with an increase in the rigidity of macromolecules, the average length of chains outside the crystalline formations decreases, and as the length of the segment is approached, the elasticity of polymer chains decreases. The crystallinity of modified copolymers is indirectly measured by the elastic modulus. As the content of 3,5-dibromo-4-hydroxybenzoic acid chloride units increases from 1 to 10 mol%, the elastic modulus increases, which is evidence of a greater crystallization tendency.

The results of thermogravimetric analysis showed that the presence of this modifier of an increase in the temperature of thermal oxidative destruction (table). The maximum decomposition temperature corresponds to 10 mol.% Of the content of the modifying additive. Such an increase in the thermal stability of modified copolymers based on 3,3-bis-(4-hydroxyphenyl) phthalide can be explained by the ordering of the supramolecular structure due to the introduction into the polymer chain of an additional aromatic ring containing a hydroxyl group in the para-position, which creates the formation of a straight rigid chain with longer. In addition, polar bromine atoms exhibit a stabilizing effect, which consists in inhibiting the chain forces of destruction of radical peroxides and deactivation of free radicals.

With an increase in the content of units of 3,5-dibromo-4-hydroxybenzoic acid in the copolymers, a decrease in thermal destruction occurs. This, most likely, is associated with the use of factors: loosening of its molecular weight, loosening of the supramolecular structure, and the increasing size of the terminal reactive groups, which can act as initiators of thermal destruction. Modified polyesters do not form droplets of ignition during combustion, i.e. are not secondary new ignitions.

The analysis of the results of the fire resistance of the synthesized polyesters showed that the values of the oxygen index (OI) are increased by the degree of increase in the content of 3,5-dibromo-4-hydroxybenzoic acid chloride units in the polymer chain. The sharp increase in the CI of polyesters provides only up to 60 mol.% Of the content of the inhibiting additive, further stabilizing. All synthesized polyesters are sufficiently stable in dilute solutions of acids and alkalis.

4. Conclusions

Progress in new areas of science and technology, the creation of products with required characteristics, transition from traditional materials to the use of new, multifunctional, can be achieved by creating materials with a variable set of properties.
Thus, for the modification of polyester based on 3,3-bis- (4-hydroxyphenyl) phthalide, a brominated derivative of 4-hydroxybenzoic acid was used in this work. These monomers are highly active under the conditions of acceptor-catalytic polycondensation. It has been shown that the introduction of 3,5-dibromo-4-hydroxybenzoic acid into the structure of a polyester based on residues of an acid chloride significantly increases the solubility of the polymer, which makes it possible to obtain soluble polyesters, and increases heat resistance and fire resistance. It follows from all that has been said that polyesters modified with 3,5-dibromo-4-hydroxybenzoic acid chloride are heat- and fire-resistant high-strength polymers that can be used in various industries as non-flammable heat-resistant structural polymer materials.

Acknowledgments
The reported study was funded by RFBR according to the research project № 18-29-18063.

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