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Polyoxadiazole Fibers Modified by Nano-Additives

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Abstract—A method of increasing the oxygen index (OI) of polyoxadiazole fibers by introducing fire retardant nano(micro)-additives into the polymer before the fiber formation is presented. The following additives are studied: dicarboxydiphenyl oxide, brominated and chlorinated phthalocianines, and carbon black. The use of these additives in the amount of 2–5% of the polymer weight in spinning solutions makes it possible to produce fibers with OI of up to 34 % and thermal stability of up to 84%.

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Polyoxadiazole fibers and their unique production technology were developed as far back as in the Soviet Union. At present such fibers, remaining a low-tonnage product, are industrially manufactured in the Republic of Belarus at Khimvolokno RUP SPO (Republic Unitary Enterprise, Svetlogosrk Production Association) under the brand name of Arselon and find application in different technical areas.

Polyoxadiazole fibers belong to the class of thermostable fibers [1, 2] and can withstand long-term service at a temperature of 230–250°C and higher. The fibers of this type do not melt; the temperature of their thermal degradation exceeds 470–480°C; the fibers are capable of carbonization with a high yield of the carbon product [3, 4]. The disadvantage of polyoxadiazole fibers is their low oxygen index, as a rule, not exceeding 27–28%. It should be noted that the data on the oxygen index of polyoxadiazole fibers (and other types of thermostable and hardly flammable fibers) are quite contradictory; the presented values range from 22 to 32% and more [1, 2, 5–8]. Apparently, in many cases the spread in the oxygen index values is related to ambiguity of methods for evaluation of this indicator. Such ambiguity exists even when experiments are carried out in full compliance with the State Standard GOST 21793-76: Methodology for Oxygen Index Determination.

In our opinion, the most appropriate approach to evaluation of the oxygen index of polymer fibrous materials and, in particular, polyoxadiazole fibers is the performance of experiments under strictly identical conditions with the use of the standardized sample preparation methodology taking into account the samples weight, density, moisture content, draw ratio etc. [9].

As an indicator of the fibers flammability, the oxygen index is determined by the chemical and supramolecular structure of the fibers, as well as by the presence of antipyrene additives, i.e. fire retardants, in their composition [10, 11]. There are several methods to increase fire-resistance of textile fibers and materials on their basis. One of the methods is synthesis of fire-resistant fiber-forming polymers; another technique is based on modification of well-known fiber-forming polymers by introducing various additives into their solutions or melts before the fiber formation. A third approach, which is relatively new, is related to modification of fibers at the moment of their formation, for example, using the polymer crazing method. A fourth method to provide textile materials with fire-resistant properties, which is rather widely used, involves modification of the finished natural or chemical fibers.

The most widespread methods for today, aimed to reduce flammability of fibers and textile materials, are based on treatment of such fibers and materials with fire retardants [12]. These methods can be divided into several groups, depending on the mechanism of the fire retardant fixation on the surface or in the structure of the fibers. In some cases it is possible to fix fire-retardant agents on the surface of the fibers using a chemical method of polymer-analogous transformations [13]. Sometimes the yarn is covered with a protective coating in the form of a film [14]. However, in the majority of cases fire retardants attach themselves to fibers by means of weak physical interactions in the course of the material impregnation with fire-retarding chemicals. It is a simple and cheap method, which is, however, inefficient for products designed for long and repeated service. Also, there are ways to reduce flammability of the finished fibers by means of physical interactions, including radiation crosslinking [15], thermal treatment [16], and thermal stretching [9]. These methods have not found wide application, as well as the polymer crazing method, which is, apparently, related to insufficient development of technologies and absence of special equipment [17]. An attempt to synthesize halogen-containing derivatives of polyoxadiazoles aimed to produce fibers with reduced flammability on their basis has not lead to significant results as well [15–18].

As indicated above, the most promising method to reduce flammability is by introducing fire-retardant additives into the structure of the polymer. It showed good results when implemented in practice: there was an increase in fire-resistance of both block polymers and certain types of fibers (polyester and polyolefin) [19, 20]. Fire-retardant additives can be introduced both into polymers melts and solutions before the formation of fibers and manufacturing of products. Such fire-retardant additives can be represented by solutions of organic and inorganic substances [21], polymer materials (for example, fluoropolymers), solid dispersed materials of different nature, and microcapsules [22]. The disadvantage of almost all methods to introduce fire retardants into polymers before the formation of products is the necessity to use fire-retardant additives in significant quantities (from 10 to 30%), which often greatly reduces physical and mechanical quality indicators of the finished products.

A new and currently poorly developed method for modification of polymer materials is based on introduction of nano-additives (particles size below 100 nm) into their structure. Such additives are represented by nanodispersed salts, metal oxides, and such carbon particles as carbon black, fullerenes, and nanotubes [23, 24]. Small size of fire retardant particles and a high specific surface area resulting from their uniform distribution in the polymer volume should contribute to an increase in fire-resistant properties even in case of reduced concentrations of fire retardants in the polymers.

The main objective of the present work is to identify possibilities to increase the oxygen index of fibers and Arselon filaments formed from poly-p-phenylene-1,3,4-oxadiazole by introducing macro- and nanodispersed additives of different nature into the polymer structure before the fiber formation.

Polyoxadiazole fibers are formed from 5–6% polymer solutions in 98% sulfuric acid. Precipitation of spinning solutions is carried out in a bath containing 72% sulfuric acid. Newly-formed fibers (filaments) are washed successively with sodium bicarbonate solution and water, dried, and subjected to thermal stretching.

In accordance with the specified task it was necessary to search for fire-retardant additives complying with the following requirements:

– resistance to the effects of concentrated sulfuric acid and its aqueous solutions;

– good solubility or dispersibility in sulfuric acid and polyoxadiazole solutions in sulfuric acid;

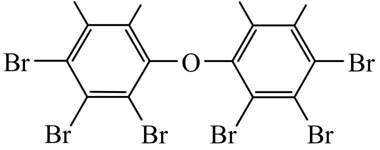
– strong fixation in the structure of polymer fibers and absence of diffusion (outwashing) in the processes of coagulation, neutralization and, washing;

– preservation of properties after short-term exposure to temperatures of 400–500°C in the course of thermal stretching of fibers;

– additives should not eventually cause a reduction in physical and mechanical properties of the finished fibers;

– fire-retardant additives should be available and cheap.

As a result of preliminary experiments the following compounds were chosen as fire-retardant additives: decabromodiphenyl oxide **I** (conventionally referred to as FR1); brominated phthalocyanine **II** (conventionally referred to as FR2); chlorinated phthalocyanine **III** (conventionally referred to as FR3); and furnace carbon black P803, low active (conventionally referred to as FR 4).



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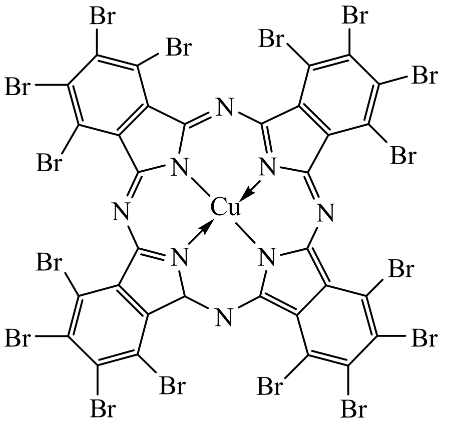

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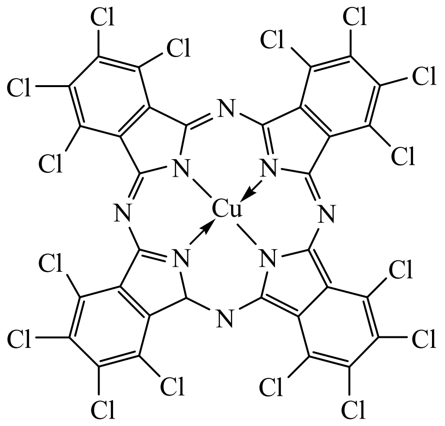

III

The basic properties of the fire-retardant additives are given in Table 1.

In order to identify specific features of thermal degradation of the fire-retardant additives and materials from poly-*p*-phenylene-1,3,4-oxadiazole derivatographic studies were performed (MOM derivatograph, Hungary; samples heated in air medium from 20 to 800°C at a rate of 5°C/min). The obtained data are given in Table 2.

The results of the experiments demonstrate that intensive burning (thermal degradation) of polyoxadiazole fibers takes place at a temperature of 450°C, while FR1, FR2, and FR3 additives decompose at temperatures 340, 400, and 450°C, respectively. Thermal degradation of the studied fire-retardant additives shortly before the start of combustion of poly-p-phenylene-1,3,4-oxadiazole should contribute to preservation of the structure of polymer materials, i.e. such additives can serve as good fire-retardant agents with respect to Arselon fibers.

Carbon black (FR4 additive) starts losing weight (burning) intensively in oxygen environment at a temperature of 500°C and maintains 5–7% of its mass

Table 1. Properties of fire retardants for modification of polyoxadiazole fibers

Fire retardant, conventional symbol[a]	Thermal stability, °C[b]	Particle size[a]	Solubility		Diffusion of fire retardant particles from polymer in formation process
			in water[c]	in conc. H_2SO_4[c]	
FR1	up to 307	> 4.7 μm	i/s	i/s	No
FR2	up to 300	< 100 nm	i/s	p/s	″
FR3	up to 350	< 100 nm	i/s	p/s	″
FR4	up to 450	80–100 nm	i/s	i/s	″

[a] See chemical nature in the text. [b] According to the manufacturers' data. [c] (i/s) Insoluble, (p/s) partially soluble.

Table 2. Results of derivational studies of polyoxadiazole fibers and fire retardants FR1···FR4

Sample	Weight loss, % at temperature, °C								Weight loss starting temperature, °C
	100	200	300	400	500	600	700	800	
Fiber	2	3	3	5	35	48	57	65	450
FR1	2	3	4	82	100	–	–	–	340
FR2	6	10	12	16	25	52	68	95	400
FR3	6	9	11	16	22	45	60	90	450
FR4	3	5	6	8	10	42	70	95	500

Table 3. Characteristics of polyoxadiazole filaments modified by fire-retardant nano-additives

Properties of filaments	Type of additive				
	no additive	FR1	FR2	FR3	FR4
Actual linear density, tex	149.0	150.8	145.0	132.0	145.0
Conditional linear density, tex	144.1	146.2	143.0	130.0	142.0
Breaking load, N	53±10	56±10	49±10	25±10	52±10
Breaking tenacity, mN/tex	365±10	377±12	372±10	363±12	360±10
Breaking elongation, %	16.0±0.4	17.0±0.4	17.0±2	18.0±2	17.4±2
Thermal stability, %	55±3	70±4	78±4	56±4	84±4
Oxygen index, %	24±2	29±3	32±2	26±2	30±2

even at a temperature of 900°C. This additive is relatively thermostable and it can be expected that its presence in the composition of the polymer will increase its thermal stability. However, the presence of carbon nanoparticles in polymer solutions and melts can cause structuring of the polymer at the moment of coagulation in the precipitation bath, which will affect the properties of the polymer fiber.

Testing of polyoxadiazole fibers, obtained from the polymer, on an experimental forming unit gave the following results (Table 3). Strength characteristics of the experimental samples are at the benchmark level at average. Breaking elongation of filaments with fire-retardant additives is a little higher as compared to standard samples. Thermal stability of the modified fibers is higher and significantly higher as compared to standard filaments. The oxygen index lies within a range of 26–34%, which significantly exceeds similar indicator for filaments without additives.

The performed studies demonstrated that the use of the selected modifying additives made it possible to obtain new generation Arselon filaments with the increased thermal stability of up to 84% and oxygen index of up to 34%.

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