SYNTHESIS AND PROCESSING OF POLYMERS AND POLYMERIC COMPOSITES

СИНТЕЗ И ПЕРЕРАБОТКА ПОЛИМЕРОВ И КОМПОЗИТОВ НА ИХ ОСНОВЕ

ISSN 2686-7575 (Online)
https://doi.org/10.32362/2410-6593-2023-18-3-243-253
UDC 544.43

RESEARCH ARTICLE

Modification of accelerated thermal stabilization of polyacrylonitrile fibers by creating an oxygen concentration gradient in the production of carbon fiber

Evgeny A. Trofimenko✉, Tatyana V. Bukharkina, Svetlana V. Verzhichinskaya

Mendeleev University of Chemical Technology of Russia, Moscow, 125047 Russia
✉Corresponding author, e-mail: e.trofimencko2016@yandex.ru

Abstract

Objectives. *The work set out to modify the technology of accelerated thermal stabilization of polyacrylonitrile (PAN) fibers used in the production of high-strength carbon fibers by reducing the formation of a heterophase core–shell structure to create an oxygen concentration gradient in heat treatment furnaces while maintaining a total thermal stabilization time of 30 min. The optimized process conditions led to milder thermal stabilization conditions, reducing both the final heat treatment temperature and the temperature difference between the thermal stabilization zones while simultaneously maintaining the target volume density parameter with respect to the previously developed accelerated thermal stabilization technology.*

Methods. *The thermal stabilization study of an industrially produced 12S precursor under different conditions on an experimental carbon fiber production line included measurement of bulk density, analysis of the thermal effects of the oxidation reaction by differential scanning calorimetry (DSC), and a study of micrographs of the resulting samples.*

Results. *The optimum process of thermal stabilization of PAN fiber was determined in four stabilization zones using selected compositions. The formation of the core–shell structure is significantly reduced when the target volume density and DSC thermal oxidation reaction effect of the stabilized polymer fiber are achieved in a given time (30 min).*

Conclusions. *The resulting technology regime is promising for the production of high strength (4.5 GPa, 4.9 GPa) PAN fibers at a reduced cost. While maintaining the total thermal stabilization time of PAN at the level of 30 min, which is three times less than the industrial processes used, it was possible to reduce the formation of a heterophase structure, as well as lowering the final processing temperature and reducing the temperature difference between the stabilization zones. This is promising in terms of a positive effect on the stability and safety of the industrial process, as well as ensuring the quality of the obtained products.*

Keywords: *composites, polyacrylonitrile, carbon fibers, stabilization, carbonation*

For citation: Trofimenko E.A., Bukharkina T.V., Verzhichinskaya S.V. Modification of accelerated thermal stabilization of polyacrylonitrile fibers by creating an oxygen concentration gradient in the production of carbon fiber. *Tonk. Khim. Tekhnol. = Fine Chem. Technol*. 2023;18(3):243–253 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2023-18-3-243-253

НАУЧНАЯ СТАТЬЯ

Модификация ускоренной термостабилизации полиакрилонитрильных волокон созданием градиента концентрации кислорода при получении углеродного волокна

Е.А. Трофименко✉, Т.В. Бухаркина, С.В. Вержичинская

Российский химико-технологический университет им. Д.И. Менделеева, Москва, 125047 Россия

✉*Автор для переписки, e-mail: e.trofimencko2016@yandex.ru*

Аннотация

Цели. *Модифицировать технологию ускоренной термостабилизации полиакрилонитрильного (ПАН) волокна при производстве высокопрочных углеродных волокон, при помощи которой удастся уменьшить образование гетерофазной структуры «ядро–оболочка» путем создания градиента концентрации кислорода в печах термообработки при сохранении общего времени термостабилизации ПАН (30 мин); оптимизировать процесс на основании предлагаемого режима с целью получения более мягких условий термостабилизации: снижения конечной температуры термообработки и разницы температур между зонами термостабилизации при сохранении целевого параметра объемной плотности (относительно ранее разработанной технологии ускоренной термостабилизации).*

Методы. *Термостабилизация промышленно выпускаемого прекурсора марки 12S в различных условиях на опытной линии получения углеродных волокон, последующее измерение объемной плотности, анализ тепловых эффектов реакции окисления методом дифференциальной сканирующей калориметрии (ДСК) и изучение микрофотографий шлифов получаемых образцов.*

Результаты. *Определен оптимальный процесс термостабилизации ПАН волокна в 4 зонах стабилизации с использованием подобранных составов, при котором существенно снижается образование структуры «ядро–оболочка» при достижении целевой обемной плотности и теплового эффекта реакции окисления ДСК стабилизируемого полимерного волокна за установленное время (30 мин).*
Выводы. *Полученный технологический режим является перспективным для получения высокопрочных (4.5 ГПа, 4.9 ГПа) ПАН волокон со сниженной себестоимостью. При сохранении общего времени термостабилизации ПАН на уровне 30 мин, что в 3 раза меньше используемых промышленных процессов, удалось снизить образование гетерофазной структуры, уменьшить конечную температуру обработки и снизить перепад температур между зонами стабилизации, что должно положительно сказаться на стабильности и безопасности ведения промышленного процесса и качестве получаемой продукции.*

Ключевые слова: *композиты, полиакрилонитрил, углеродные волокна, стабилизация, карбонизация*

Для цитирования: Трофименко Е.А., Бухаркина Т.В., Вержичинская С.В. Модификация ускоренной термостабилизации полиакрилонитрильных волокон созданием градиента концентрации кислорода при получении углеродного волокна. *Тонкие химические технологии*. 2023;18(3):243–253. https://doi.org/10.32362/2410-6593-2023-18-3-243-253

INTRODUCTION

The development of technologies for reducing the cost of carbon fiber (CF) production is one of the most significant directions in the industry today. Rather than aiming at the production of ultrahigh-strength products (4.5 GPa or more), such technologies are geared to the satisfaction of mass market demand. With a significant reduction in cost, fibers with a strength of 4.0–4.2 GPa will be in greater demand in the automotive, sports equipment, construction, shipbuilding, and wind energy industries, helping to stimulate the development of new design solutions in these industries and increasing the introduction of carbon composites into everyday life.

The total cost of producing a kilogram of CF is made up of many factors. These include the price of precursors (acrylonitrile, methyl acrylate, itaconic acid, etc.), the price of solvents for the commonly-used wet molding method (zinc chloride, dimethylacetamide, sodium thiocyanate, etc.), the price of auxiliary chemicals (oiling agents, antistatic agents, and dressing compositions), depreciation costs for expensive equipment, and electricity, large quantities of which are used in the main (synthesis, molding, and heat treatment) and auxiliary technological processes (solvent regeneration).

In connection with the above factors, work is underway to improve the efficiency of associated processes and thus reduce costs. The present work considers the heat treatment of polyacrylonitrile (PAN) to obtain desired hydrocarbon products. In our previously published works, proposals for modifying traditional CF production technology in order to reduce the time of thermal stabilization of the fiber prior to carbonization were presented and substantiated [1–3]. By pre-stabilizing the PAN fiber in nitrogen, followed by oxidation of the pre-stabilized fibers, the process time was reduced to 30 min without any loss of product quality. A comparison of the proposed system with classic industrial technology based on the oxidation process alone shows a three-fold reduction in thermal stabilization time. At the same time, the strength of the fibers obtained is in the order of 4.3 GPa, while the modulus of elasticity is around 240 GPa. Using the nominal value of 12K (12000 monofilaments), it was possible to maintain the standard linear

density of 785 tex (g/km) for this type of fiber, which is an extremely important indicator in industrial production [1,2,3,4].

An industrial line developed on the basis of the described technology offers a 2.5–3 times increase in the speed of fiber passage as compared to current industrial processes. A corresponding 40% reduction in the cost of CF production would represent a serious incentive for the development of the composites industry.

However, despite sufficient results in terms of mechanical tests and cost-benefit assessment, the technology proposed by the present authors in [1–3] involves a number of drawbacks:

– a high (up to 20°C) temperature difference between the furnace zones, representing a source of production concern, since such a temperature jump can lead to uncontrolled local overheating of the fiber due to exothermic reactions on its surface. This effect can lead to fiber breakage in an industrial furnace, increasing scrap yields and downtime on the refueling line;

– the formation of a heterophase core–shell structure, resulting in reduced physical and mechanical properties of the fiber at the heat treatment stage.

Thus, the present work continues the development of accelerated thermal stabilization processes in an attempt to eliminate these two serious shortcomings in the presented CF production technology.

Experience with accelerated oxidation has shown that PAN fibers become extremely reactive after being pre-stabilized in nitrogen, leading to very rapid reactions with atmospheric oxygen when entering the oxidation furnace. On the one hand, such high reactivity can be useful when intensifying the process, including a reduction in total stabilization time and the number of required furnaces to four (the standard scheme of heat treatment in air includes 6–8 oxidation furnaces [4–6]). On the other hand, such rapid reactions—even those occurring at relatively low temperatures—lead to the formation of a shell of more stabilized PAN on the surface of the monofilament, which is poorly permeable to the gases (particularly oxygen) used for the thermal stabilization reactions in the formed core. Due to the appearance of such a shell, it becomes necessary to significantly increase the temperature in the subsequent zones in order to bring the final volume density of the stabilized fiber to 1.36 g/cm^3 (the minimum density value sufficient for safe carbonization of the fiber) [7, 8]. As a result, two distinct phases are distinguished depending on the radius of the monofilament: core and sheath. A less dense core lacks stability and may partially degrade during carbonization, leading to a reduction in the physical and mechanical properties of the final CF.

Despite previous work aimed at identifying heat treatment modes for minimizing this negative effect, it was not possible to eliminate it completely [2]: a significant increase in the temperature difference between the zones continues to be necessary for maintaining the core–shell effect.

To reduce this effect along with the temperature difference between the zones to at least 10°C, a series of experiments with a gradient of oxygen concentration between the zones was proposed (hereafter referred to as the "Gradient experiment"). The essence of these experiments was to reduce the formation of a gas-tight shell on the surface of the filament in the early stages of oxidation by reducing its rate without increasing the temperature gradient. Taking into account studies [9–11], the use of stabilization in nitrogen (or in a rarefied atmosphere) increases the yield of carbon fibers, which also improves the productivity of CF production lines and associated economic factors. Therefore, the first stage of oxidation following prestabilization in nitrogen was carried out in an oxygen-depleted environment. Here, it was assumed that the reduced oxygen concentration would intensify the formation of a heterophase structure, which would slightly increase its diffusion towards the center of the monofilament to improve the volume density set.

In the first stages of the study, the thermal stabilization parameters—in particular, the temperature and oxygen concentration in the specified heat treatment zone—were determined. The oxidation conditions in the subsequent zones were selected on the basis of the fiber properties.

MATERIALS AND METHODS

The methods used to develop and study the samples are described in the article [2]. All work and experiments were carried out at the *YUMATEKS* research center, which is part of the

[1] https://www.torayca.com/en/download/. Accessed August 10, 2022.

[2] https://umatex.com/production/fiber/. Accessed August 10, 2022.

[3] https://www.dowaksa.com/aksaca/. Accessed August 10, 2022.

[4] https://www.teijincarbon.com/ru/produkcija/uglerodnye-volokna-tenaxr/zhguty-tenaxr/. Accessed August 10, 2022.

New Materials and Technologies division of the *Rosatom* company group (Russia). The research center is equipped with an experimental line for the CF production, comprising a set of 6 three-pass oxidation furnaces, a low temperature carbonization (LTC) furnace, a high temperature carbonization (HTC) furnace, a surface treatment module, as well as receiving equipment. In addition, the line is equipped with the necessary ancillary equipment, starting with a nitrogen station for operations involving high purity nitrogen (>99.9999%). The exothermic effect of the oxidation reaction of PAN samples stabilized to different densities was determined using a DSC214 differential scanning calorimeter (*Netzsch*, Germany). An RR/DGA gradient column (*Ray-Ran Test Equipment*, United Kingdom) was used to determine the changes in bulk density of the material as a function of heat treatment conditions. A Tegramin-20 grinding system (*Struers*, France) and Olympus BX-51 microscope with U-TV0.63XC camera (*Olympus*, Japan) were used for the comparative evaluation of the formation of heterophase core–shell structures in samples developed by classical accelerated oxidation for the development of the stages of the experimental gradient mode.

As in previous experiments, the industrially produced PAN precursor Jilin 12k was used as the base precursor. Until recently, this was the fiber used at *ALABUGA-Volokno*, the largest enterprise in Russia for CF production. Based on the characteristics and parameters of this PAN, it is possible to obtain industrial quantities of hydrocarbons having a strength of 4.5 GPa, a modulus of elasticity of 250 GPa, and a linear density of 800 ± 20 tex, representing a considerable CF market niche.

The PAN harness was pre-stabilized in a high purity nitrogen medium using an LTC furnace. The experimental line for the CF production transport system was used to create continuous fiber movement through a nitrogen-blown carbonation furnace. At the same time, the operation of the transport system was organized in such a way as to ensure that the fiber remained in the working chamber of the furnace for 10 min at a temperature of 255°C. This unchanged parameter was accepted as optimal according to the results of previous studies [1, 2]. After winding the pre-stabilized fiber onto the spool using an automatic take-up device, it was mounted onto the feed spool for unwinding the fiber and passing it through the heat stabilization zones.

To function as a reduced oxygen thermal stabilization chamber, one of the oxidation furnaces was selected. Since there was no requirement for connecting gases other than atmospheric air during the design and construction of these furnaces, a new connection was made via a fitting inserted into the atmospheric air inlet pipe below the level of the adjustable valve. Pipes were then laid from the nitrogen station to the oxidation furnaces to supply the system with inert gas. At the nitrogen station itself, the gas supply system was split between the LTC and HTC furnaces, as well as, separately, to the oxidation furnace. A regulator installed between the nitrogen station's gasifier and the pipes leading to the oxidation furnaces was used to maintain the nitrogen supply pressure at 3 atm. In order to ensure the required level of purity, a 150 L/min capacity rotameter was used to regulate the flow of supplied nitrogen; this was installed at the end of the system before the nitrogen is supplied to the oxidation furnace No. 1 (OF1). Immediately prior to commencing the process, the ambient air inlet valve was closed and the nitrogen consumption was increased at the rotameter. The nitrogen concentration in OF1 was monitored using an external oxygen analyzer SGM7T (*Zirox*, Germany), whose inlet tube was placed in the working area of the furnace. By changing the nitrogen consumption at the rotameter, the composition of the medium can be controlled by the gas analyzer to achieve the required oxygen content in the working atmosphere.

Similar changes only affected OF1. The remaining zones of thermal stabilization (oxidation furnaces OF2 and OF3) operated in normal mode without additional supply of inert gas.

The transport system provided the same fiber dwell time (6.6 min) in each of the three OF1–OF3 zones. The total residence time of the fiber in the heat treatment zone, taking into account the time of pre-stabilization in nitrogen and subsequent treatment in oxidation furnaces, was ~30 min.

The samples were produced at different temperatures in OF1–OF3 and different (5.5 and 11%) oxygen concentrations in OF1.

The samples obtained from the Gradient experiment were analyzed on the DSC214 and compared with differential scanning calorimetry (DSC) data obtained in accelerated oxidation mode. The bulk density of the samples and the appearance of the monofilament were analyzed under a microscope at different processing stages.

RESULTS AND DISCUSSION

Since the density of the nitrogen pre-stabilized fiber was 1.225 g/cm^3, in order to achieve a bulk density ≥1.36 g/cm^3, it becomes necessary to

increase the fiber density in each of the three following zones by at least 0.045 g/cm^3.

The installed OF1 nitrogen supply system created a working atmosphere with an oxygen content of 5.37–5.49%, which is close enough to the target. The temperature in the furnace was raised to 240°C. Based on the results of the density measurement following heat treatment in OF1, it was decided to change the temperature. The results of the selection of the working conditions of OF1 are presented in Table 1 along with the data on the measurement of the bulk density of the obtained samples and the thermal effects of the DSC reaction in air (ΔH_{ox}).

The characteristics of Samples 3 and 4, which were developed at temperatures of 250 and 260°C, respectively, are close to those of reference Sample 6 (Table 1).

Figure 1 shows the sections of the micrographs of the samples developed according to the modes shown in Table 1 modes (also included is the micrograph of the reference sample with standard accelerated oxidation).

From Figure 1, it can be seen that an oxygen concentration gradient in the OF1 and OF2 furnaces results in a significantly less pronounced core–shell structure along with comparable values of volume density and thermal oxidation effects as measured by DSC. While the presence of such a structure is not in itself a limiting factor in obtaining high quality fibers, it is associated with high filament surface reactivity, which prevents the diffusion of oxygen into the central part of the elementary fiber [12].

In the second stage of the experiment, the change in fiber parameters was analyzed at different processing temperatures in a working environment with an oxygen concentration of 11%. The results of the selection of conditions in OF1 are shown in Table 2.

It is worth noting that, at a concentration of 11% and increasing temperature, the change in ΔH_{ox} passes through the minimum point (Sample 2), after which it begins to increase. As confirmed by the developed heterophase structure of the samples shown in Fig. 2, this may be explained in terms of the extremely rapid formation of the core–shell structure at high temperatures and an increased oxygen content in the process atmosphere as compared to the previous series of experiments.

From the presented comparative data, it can be concluded that the use of an 11% oxygen regime in OF1 is less promising since it does not prevent the formation of a heterophase structure. A further selection of modes was made at an oxygen concentration of 5.5%. The volume density of stabilized PAN closest to the target was obtained at a temperature of 260°C. This temperature in OF1 was used for future process development.

The process conditions in OF2 and OF3 were selected sequentially. The results of the calculation of OF2 working conditions are presented in Table 3.

The closest properties to the required bulk density were found at a temperature of 260°C. The ensuing fiber was highly manufacturable, without damaged filaments or damaged harness areas. To test the heat treatment conditions

Table 1. Results of the heat treatment mode selection in OF1 at an oxygen concentration of ~5.5%

Number of sample	Temperature T_{OF1}, °C	Density ρ, g/cm^3	ΔH_{ox}, J/g
1	240	1.2445	1282
2	245	1.2456	1266
3	250	1.2581	1110
4	260	1.2676	1096
5	270	1.2786	1069
6*	240	1.2580	1016

*This sample is a sample for comparison. Its properties are typical of the fiber after the first oxidation zone according to the accelerated oxidation mode presented in [2]—standard accelerated oxidation.

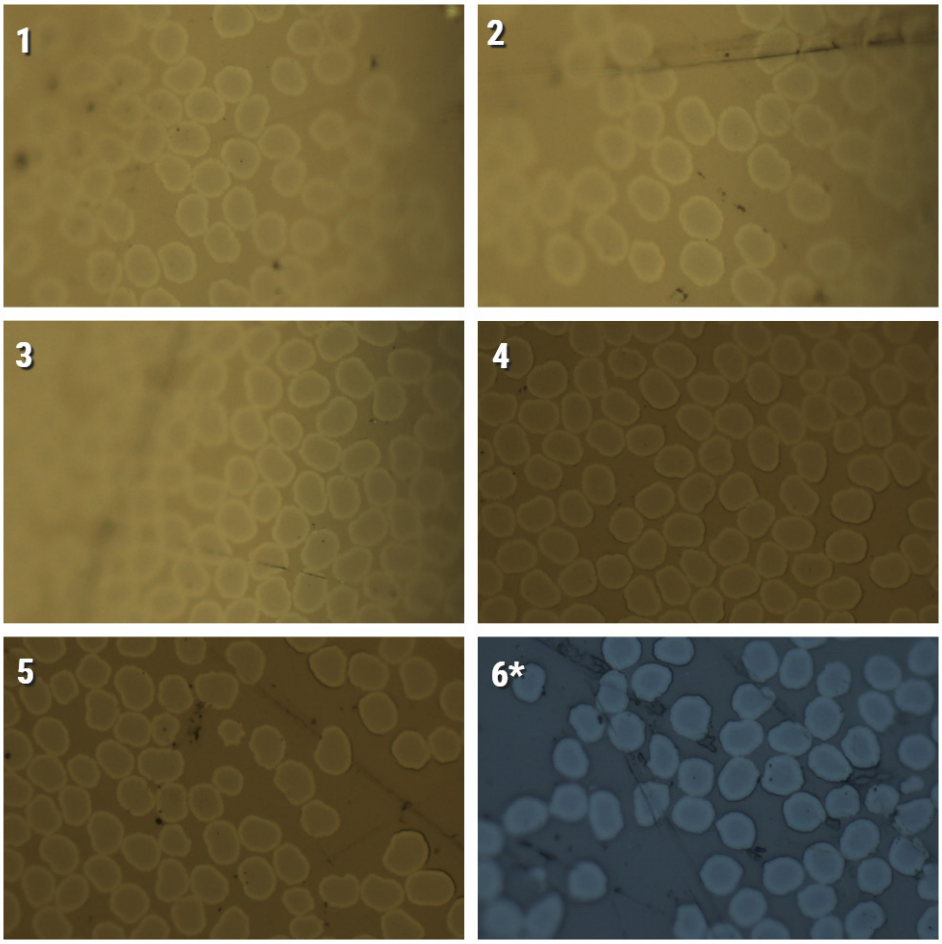

Fig. 1. Photomicrographs of fiber samples stabilized at different temperatures in an oxygen concentration of 5.5% in OF1: 1 – 240°C, 2 – 245°C, 3 – 250°C, 4 – 260°C, 5 – 270°C, and 6* – comparison sample.

Table 2. Results of the heat treatment mode selection in OF1 at an oxygen concentration of ~11%

Number of sample	Temperature T_{OF1}, °C	Density ρ, g/cm^3	ΔH_{ox}, J/g
1	240	1.249	1081
2	245	1.260	929
3	250	1.267	950
4	255	1.273	1060
5	260	1.283	1141
6	270	1.301	1297
7*	240	1.258	1016

*This sample is a sample for comparison.

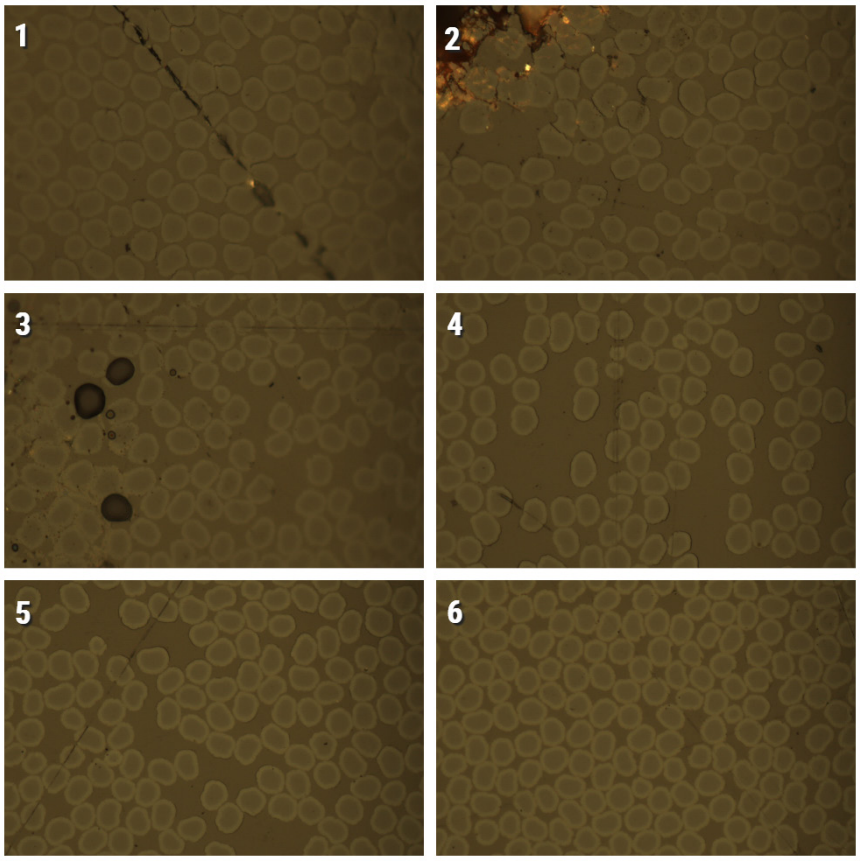

Fig. 2. Photomicrographs of samples of fibers stabilized at different temperatures in an oxygen concentration of 11% in OF1: 1 – 240°C, 2 – 245°C, 3 – 250°C, 4 – 255°C, 5 – 260°C, and 6 – 270°C.

in the OF3 zone, the OF2 temperature was fixed at 260°C. The results of the selection of conditions for OF3 are shown in Table 4.

A bulk density above the required value of 1.36 g/cm^3 was achieved at a process temperature of 270°C in the final thermal stabilization zone. The high manufacturability of the harness at the exit of the oxidation zones was also noted. Moreover, the smaller size of the shell in the heterophase structure, having comparable values of linear density and thermal effect of the oxidation reaction according to DSC, may indicate higher core stability (Fig. 3).

Table 3. Results of the heat treatment mode selection in OF2

Number of sample	Temperature T_{OF2}, °C	Density ρ, g/cm^3
1	210	1.2855
2	220	1.2848
3	230	1.2910
4	240	1.3002
5	250	1.3192
6	260	1.3309

Table 4. Results of the heat treatment mode selection in OF3

Number of sample	Temperature T_{OF3}, °C	Density ρ, g/cm^3	ΔH_{ox}, J/g
1	250	1.3380	874
2	255	1.3405	856
3	260	1.3498	848
4	265	1.3547	861
5	270	1.3616	754
6*	280	1.3672	715

*This sample is a sample for comparison.

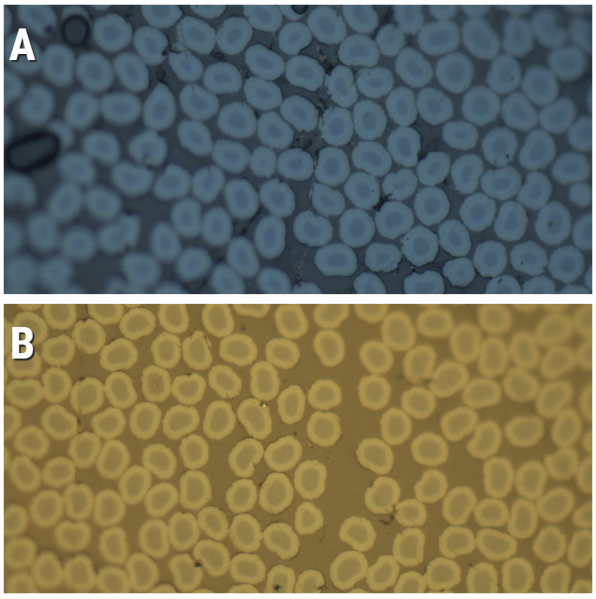

Fig. 3. Comparison of stabilized fiber pulps using standard accelerated thermal stabilization technology (A) [2] and the results of the Gradient experiment (B).

While the main disadvantage of the proposed solution is its increased nitrogen consumption, this problem can be partially solved on an industrial line by recovering part of the nitrogen from the pre-stabilization zone and returning it to the OF1 zone.

CONCLUSIONS

The experiments demonstrated that an atmosphere with a depleted oxygen content in OF1 can be used to reduce the formation of a heterophase structure and obtain a more stable fiber core while maintaining a pre-stabilization zone in nitrogen. The temperature profile of the thermal stabilization process proposed in the described Gradient experiment has advantages over the classical accelerated stabilization process considered by the authors in previous works. The 10°C lower final temperature of the heat treatment and reduced temperature difference (<10°C) between two adjacent stages of thermal stabilization helps to prevent damage and fiber breakage on the processing line by significantly reducing the risk of local overheating. This is particularly important when factory CF production lines are operated in canvas mode in order to increase productivity; here, the individual bundles are packed as closely together as possible, effectively forming a wide ribbon of processed material. By reducing the final processing temperature by as little as 10°C, the risk of uncontrolled exothermic overheating and spontaneous ignition of the material can be significantly reduced.

At the same time, the Gradient mode retains the main advantage of classical accelerated stabilization in terms of the short process time of 30 min. A threefold reduction in thermal stabilization time as compared to the generally accepted oxidation PAN technology provides significant savings in capital costs required to build larger workshops by reducing the number of required furnaces and overall energy consumption. In addition to the greater economic potential as compared to the generally accepted technology of oxidative stabilization, its increased safetymakes the Gradient mode promising for introduction into industrial production.

Acknowledgments

The authors thank the staff of the YUMATEX research center of Rosatom for the provided equipment and advice in determining the boundaries of technological regimes.

Authors' contributions

E.A. Trofimenko – study concept, conducting experiments, analyzing the results, and writing the text of the article.

T.V. Bukharkina – refining the structure of experiments, analyzing the results, and developing the concept of further study.

T.V. Verzhichinskaya – analyzing the results, correcting the program of further study, and editing the article.

The authors declare no conflicts of interest.

REFERENCES

1. Trofimenko E.A., Bukharkina T.V., Verzhichinskaya S.V., Gavrilov Yu.V. Kinetic model of polyacrylonitrile fibers thermostabilization in nitrogen atmosphere. *Izvestiya vysshikh uchebnykh zavedenii. Tekhnologiya tekstil'noi promyshlennosti = Proceedings of the Higher Educational Institutions. Textile Industry Technology*. 2021;39(6):129–135 (in Russ.). https://doi.org/10.47367/0021-3497_2021_6_129

2. Trofimenko E.A., Bukharkina T.V., Verzhichinskaya S.V., Kozlovskii I.A. Accelerated stabilization of polyacrylonitrile fiber for the production high-strength carbon fibers. *Izvestiya vysshikh uchebnykh zavedenii. Tekhnologiya tekstil'noi promyshlennosti = Proceedings of the Higher Educational Institutions. Textile Industry Technology*. 2022;399(3):172–178 (in Russ.). URL: https://ttp.ivgpu.com/wp-content/uploads/2022/08/399_28.pdf. Accessed October 01, 2022.

3. Trofimenko E.A., Bukharkina T.V., Verzhichinskaya S.V., Staroverov D.V. Effect of carbonation duration during accelerated thermal stabilization of polyacrylonitrile fibers on the properties of carbon filaments. *Khimicheskaya promyshlennost' segodnya = Chemical Industry Developments*. 2022;(2):16–19 (in Russ.). https://doi.org/10.53884/27132854_2022_2_16

4. Minus M.L., Kumar S. The processing, properties, and structure of carbon fibers. *JOM*. 2005;57(2):52–58. https://doi.org/10.1007/s11837-005-0217-8

5. Warner S.B, Peebles L.H., Uhlmann D.R. Oxidative stabilization of acrylic fibers. 1. Oxygen-uptake and general-model. *J. Mater. Sci.* 1979;14(3):556–564. https://doi.org/10.1007/BF00772714

6. Rahaman M.S.A., Ismail A.F., Mustafa A. A review of heat treatment on polyacrylonitrile fiber. *Polym. Degrad. Stab*. 2007;92(8):1421–1432. https://doi.org/10.1016/j.polymdegradstab.2007.03.023

7. Jie L., Yueyi Z., Lianfeng, Zhaokun M., Jieying L. *Method for preparing high-strength carbon fiber*: China Pat. CN102154740A. Publ. 13.05.2011.

8. Cook J.D., Taylor T., Deshpande G.V., Tang L., Meece B.D., Crawford S., Chiu S.C., Harmon B.D., Thomas A. *Manufacture of intermediate modulus carbon fiber*: Pat. WO2016144488A1. Publ. 15.09.2016.

9. Qin X., Lu Y., Xiao H., Song Y. Improving stabilization degree of stabilized fibers by pretreating polyacrylonitrile precursor fibers in nitrogen. *Materials Letters*. 2012;76:162–164. https://doi.org/10.1016/j.matlet.2012.02.103

СПИСОК ЛИТЕРАТУРЫ

1. Трофименко Е.А., Бухаркина Т.В., Вержичинская С.В. Гаврилов Ю.В. Кинетическая модель термостабилизации полиакрилонитрильных волокон в атмосфере азота. *Известия высших учебных заведений. Технология текстильной промышленности*. 2021;396(6):129–135. https://doi.org/10.47367/0021-3497_2021_6_129

2. Трофименко Е.А., Бухаркина Т.В., Вержичинская С.В., Козловский И.А. Ускоренная стабилизация полиакрилонитрильного волокна для получения высокопрочных углеродных волокон. *Известия высших учебных заведений. Технология текстильной промышленности.* 2022;399(3):172–178. URL: https://ttp.ivgpu.com/wp-content/uploads/2022/08/399_28.pdf. Дата обращения 01.10.2022.

3. Трофименко Е.А., Бухаркина Т.В., Вержичинская С.В., Староверов Д.В. Влияние продолжительности карбонизации при ускоренной термостабилизации полиакрилонитрильных волокон на свойства углеродных нитей. *Химическая промышленность сегодня.* 2022;(2):16–19. https://doi.org/10.53884/27132854_2022_2_16

4. Minus M.L., Kumar S. The processing, properties, and structure of carbon fibers. *JOM*. 2005;57(2):52–58. https://doi.org/10.1007/s11837-005-0217-8

5. Warner S.B, Peebles L.H., Uhlmann D.R. Oxidative stabilization of acrylic fibers. 1. Oxygen-uptake and general-model. *J. Mater. Sci.* 1979;14(3):556–564. https://doi.org/10.1007/BF00772714

6. Rahaman M.S.A., Ismail A.F., Mustafa A. A review of heat treatment on polyacrylonitrile fiber. *Polym. Degrad. Stab*. 2007;92(8):1421–1432. https://doi.org/10.1016/j.polymdegradstab.2007.03.023

7. Jie L., Yueyi Z., Lianfeng, Zhaokun M., Jieying L. *Method for preparing high-strength carbon fiber*: Pat. CN102154740A China. Publ. 13.05.2011.

8. Cook J.D., Taylor T., Deshpande G.V., Tang L., Meece B.D., Crawford S., Chiu S.C., Harmon B.D., Thomas A. *Manufacture of intermediate modulus carbon fiber*: Pat. WO2016144488A1. Publ. 15.09.2016.

9. Qin X., Lu Y., Xiao H., Song Y. Improving stabilization degree of stabilized fibers by pretreating polyacrylonitrile precursor fibers in nitrogen. *Materials Letters*. 2012;76:162–164. https://doi.org/10.1016/j.matlet.2012.02.103

10. Atkiss S.P., Maghe M.R. *Precursor stabilisation process*: Pat. AU2022287549A1 Australia. Publ. 12.12.2022.

10. Atkiss S.P., Maghe M.R. *Precursor stabilisation process*: Australia Pat. AU2022287549A1. Publ. 12.12.2022.

11. Keller A., Fauth G., Ziegler U. *Method and device for stabilizing precursor fibers for the production of carbon fibers*: USA Pat. US11486059B2. Publ. 01.11.2020.

12. Lv M-y., Ge H-y., Chen J. Study on the chemical structure and skin-core structure of polyacrulonitrile-based fibers during stabilization. *J. Polym. Res*. 2009;16(5):513–517. https://doi.org/10.1007/s10965-008-9254-7

11. Keller A., Fauth G., Ziegler U. *Method and device for stabilizing precursor fibers for the production of carbon fibers*: Pat. US11486059B2 USA. Publ. 01.11.2020.

12. Lv M-y., Ge H-y., Chen J. Study on the chemical structure and skin-core structure of polyacrulonitrile-based fibers during stabilization. *J. Polym. Res*. 2009;16(5):513–517. https://doi.org/10.1007/s10965-008-9254-7

About the authors:

Evgeny A. Trofimenko, Postgraduate Student, Department of Chemical Technology of Natural Energy Sources and Carbon Materials, Mendeleev University of Chemical Technology of Russia (9, Miusskaya pl., Moscow, 125047, Russia). E-mail: e.trofimencko2016@yandex.ru. RSCI SPIN-code 9855-0716, https://orcid.org/0000-0003-0084-9103

Tatyana V. Bukharkina, Dr. Sci. (Chem.), Professor, Department of Chemical Technology of Natural Energy Sources and Carbon Materials, Mendeleev University of Chemical Technology of Russia (9, Miusskaya pl., Moscow, 125047, Russia). E-mail: tvb_53@mail.ru. Scopus Author ID 55925186900, RSCI SPIN-code 1138-2040

Svetlana V. Verzhichinskaya, Cand. Sci. (Chem.), Associate Professor, Department of Chemical Technology of Natural Energy Sources and Carbon Materials, Mendeleev University of Chemical Technology of Russia (9, Miusskaya pl., Moscow, 125047, Russia). E-mail: verlanasv@muctr.ru. Scopus Author ID 6504274958, RSCI SPIN-code 8957-0316

Об авторах:

Трофименко Евгений Александрович, аспирант кафедры химической технологии природных энергоносителей и углеродных материалов ФГБОУ ВО «Российский химико-технологический университет имени Д.И. Менделеева» (125047, Россия, Москва, Миусская пл., д. 9). E-mail: e.trofimencko2016@yandex.ru. SPIN-код РИНЦ 9855-0716, https://orcid.org/0000-0003-0084-9103

Бухаркина Татьяна Владимировна, д.х.н., профессор кафедры химической технологии природных энергоносителей и углеродных материалов ФГБОУ ВО «Российский химико-технологический университет имени Д.И. Менделеева» (125047, Россия, Москва, Миусская пл., д. 9). E-mail: tvb_53@mail.ru. Scopus Author ID 55925186900, SPIN-код РИНЦ 1138-2040

Вержичинская Светлана Владимировна, к.х.н., доцент кафедры химической технологии природных энергоносителей и углеродных материалов ФГБОУ ВО «Российский химико-технологический университет имени Д.И. Менделеева» (125047, Россия, Москва, Миусская пл., д. 9). E-mail: verlanasv@muctr.ru. Scopus Author ID 6504274958, SPIN-код РИНЦ 8957-0316

The article was submitted: October 07, 2022; approved after reviewing: November 15, 2022; accepted for publication: May 25, 2023.

Translated from Russian into English by N. Isaeva
Edited for English language and spelling by Thomas A. Beavitt