ISSN 2635-1676, Nanobiotechnology Reports, 2022, Vol. 17, No. 3, pp. 372–379. © Pleiades Publishing, Ltd., 2022.

FUNCTIONAL AND CONSTRUCTION NANOMATERIALS

Carbon Fibers from Cellulosic Precursor for Thermal Insulation: An Insight Into the Effect of Stabilization and Carbonization Conditions on the Synthesis

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Received August 19, 2021; revised November 28, 2021; accepted December 2, 2021

Abstract—There is an increasing demand for lightweight composites reinforced with carbon fibers (CFs) that possess exceptional thermal characteristics, especially at high-temperature conditions. The focus of this study is primarily on the sequence of structural changes at the micro-nano level during the carbonization of cellulosic fibers collected from Northern Vietnam. The impact of various operational parameters in the carbonization process such as the heating temperature and the stabilization process also discussed. The chemical structure, morphology, and thermal conductivity of cellulose-based fiber were investigated. This investigation revealed that prepared CF-3 using cellulosic fibers collected from Northern Vietnam through the optimized parameters can be a potentials material for making outer ring insulation in high-temperature furnace environments.

DOI: 10.1134/S2635167622030090

INTRODUCTION

Carbon fibers (CFs) are made up of a lengthy strand of carbon atoms linked together that have a carbon content of 90% or more [1–3]. CFs are well-known for their superior strength and light-weighting potential, making them a desirable candidate for load-bearing applications [3, 4]. The CFs industry has been steadily expanding, with a focus on aerospace, military, construction, medical, and sporting goods [1–5]. Also, CFs possesses exceptional thermal characteristics, especially in high-temperature conditions exceeding 1500°C at an inert atmosphere hence it can be used as a promising material for thermal insulation in high-temperature furnaces [6–10]. CFs could be synthesized from any fibrous polymeric precursor that can be yield carbonaceous residue during the pyrolysis process. The production of CFs begins with the spinning of raw materials and is then transformed into CFs through a two-step heat treatment: 1) oxidative stabilization (200–350°C) and carbonization (>1000°C) [4, 5, 11]. The characteristic of CFs is mainly depending on specific conditions of heat treatment and type of the raw materials used. Based on carbonization temperature, the prepared CFs can be categorized into type I (>2000°C), Type II (≥1500°C), and Type III (>1000°C) [3, 12]. Because of their high yield and good mechanical characteristics, polyacrylonitrile (PAN) precursor is mostly used to make the majority of CFs [1–6, 13, 14]. Cellulose fibers and mesophase pitch are also used to obtain CFs [15, 16]. The cost of CFs production from PAN is greatly affected by crude oil prices, causing the production cost of CFs from PAN to fluctuate which limits their widespread use in various applications. The cellulose-based CFs are preferred not only due to the low price of manufactured goods but also owing to good thermal characteristics and purity. CFs made from cellulose currently account for only 1–2 percent of total CFs production [1–5, 15].

The price of CFs must be significantly reduced to establish CFs in the mass market. Alternative natural resources for CFs should be identified and implemented in the coming years in this regard. When switching to new materials with enhanced characteristics, low-cost CFs will be required not only by the

automotive industry, but also by the construction industry, power industry, and mechanical engineering [15–18]. Due to Vietnam's current needs in terms of industrialization, modernization, and national security development, it is necessary to investigate the production of CFs and their composites for use in a variety of fields, such as: as insulation material in high-temperature furnaces or to replace coal as an insulator in MeClelland's hot press [19]. Furthermore, CFs can be used to obtain ATJ pyrolysis graphite material, which is applied in the manufacture of rocket propellers and other composite-based applications [20].

The conversion of cellulosic biomass into CFs has attracted a lot of interest worldwide due to the fast-expanding demands in producing biosourced sustainable products. However, conventional carbonization approaches have struggled to achieve CFs with outstanding quality as a result of the complex composition of cellulosic biomass. The excellence of CFs depends heavily on the pyrolysis and carbonization procedures and is not only affected by orientation, structure, composition, and quality of the precursor fiber [21–23]. Le et al specified the need to optimize the processing parameters to produce carbon fibers with superior mechanical characteristics during stabilization and carbonization [24]. Also, they highlighted that incomplete stabilized fibers can produce hollow CFS via carbonization, which might be used in batteries or membranes. By optimizing the heat treatment, Lewandowska et al were able to develop CFs with ordered graphitic-like structures from cellulose fiber precursors [25]. Wang et al. highlighted that cellulosic biomass is reductively carbonized to form activated carbon fibers for the adsorption of nonpolar organic compounds [26]. With these motivations, the current study is focused on the synthesis of type III CFs from cellulosic precursors (cotton) and study the effect of stabilization and carbonization conditions on the characteristics and thermal conductivity of the final product.

EXPERIMENTAL

Materials and Experimental Procedures

The natural cotton grown and harvested in the northern area of Vietnam (product of Hiep Hung Company, Bac Giang, Vietnam) was used as the precursor to synthesize the carbon fiber in this research.

The schematic of the preparation of CFs from cotton is shown in Fig. 1a. We have carried out the oxidation process at 200°C for 1 h and stabilized cotton in the air at 300°C for different times (1.5, 2, 2.5, and 3 h). After that, we carried out the carbonization stage of cotton in an inert gas atmosphere to a temperature of 1000°C. To know the effect of heating rate, 100, 200, 300, and 400°C/h heating rate from 300 to 1000°C are investigated. The different annealing times such as 1, 2, 3, and 4 h after carbonization were also investigated. The final product CF-3 was obtained by annealing after carbonization in an inert gas atmosphere at a temperature of 1200°C.

To prepare Type III carbon fiber (CF-3) from cellulose precursor, we have utilized equipment with simplicity, ease of use, high product recovery efficiency, low equipment depreciation, and savings protective gas in production. A LDT 1280 resistive vertical furnace used for the preparation of CFs from cotton is shown in Fig. 1b. All parts of the LDT 1280 furnace are made of SU-304 steel, except resistance wire and the insulating materials, which are made of aluminum oxide ceramic. The Argon gas is passed through the air filter to remove water vapor and oxygen. An oxygen catcher and self-regenerating steam are included in the air filter. The gas then passes through the reometer to measure and control the gas flow before being fed into the furnace. The gas going from the top makes the space in the reactor always filled, the amount of protective gas supplied to the furnace is very small during the reaction to form CF-3. The LDT 1280 furnace's gas pipe is welded to the reaction vessel. The air duct is located outside the furnace. Argon gas when going from the top of the reactor to the bottom through the initial mixture of cotton and CF-3 (formed after the reaction) to the bottom of the flask. The gas products after the reaction are passed from the bottom of the reactor which is then discharged into a fume hood to a toxic gas treatment center before being discharged into the environment.

Analytical Techniques

Cotton samples after the processes of stabilization and carbonization at different circumstances were analyzed by the X-ray diffraction diffractometer in the 2θ range of 10°–90° by using CuK_α radiation as a source with voltage and the current setting of 40 kV and 30 mA, respectively. The morphological characteristic was analyzed using a scanning Electron Microscope (SEM) and optical microscope. CF-3 fibers were structurally analyzed by the transmission Electron microscope (TEM) at the Vietnam Academy of Science and Technology. Samples were dispersed using solvents onto TEM grids and then air-dried for imaging. The composite sample is made from CF-3 carbon fiber and tested for thermal conductivity according to ASTM-C177 standard at Vilas 003 laboratory—Center for refractory and fireproof materials—Vietnam institute for building materials (VIBM).

RESULTS AND DISCUSSION

Figure 2 shows the SEM images of cotton precursors collected from Northern Vietnam with different magnification shows the morphological characteristics of cotton fiber in different length scales. It is found that cotton precursors have a smooth surface with

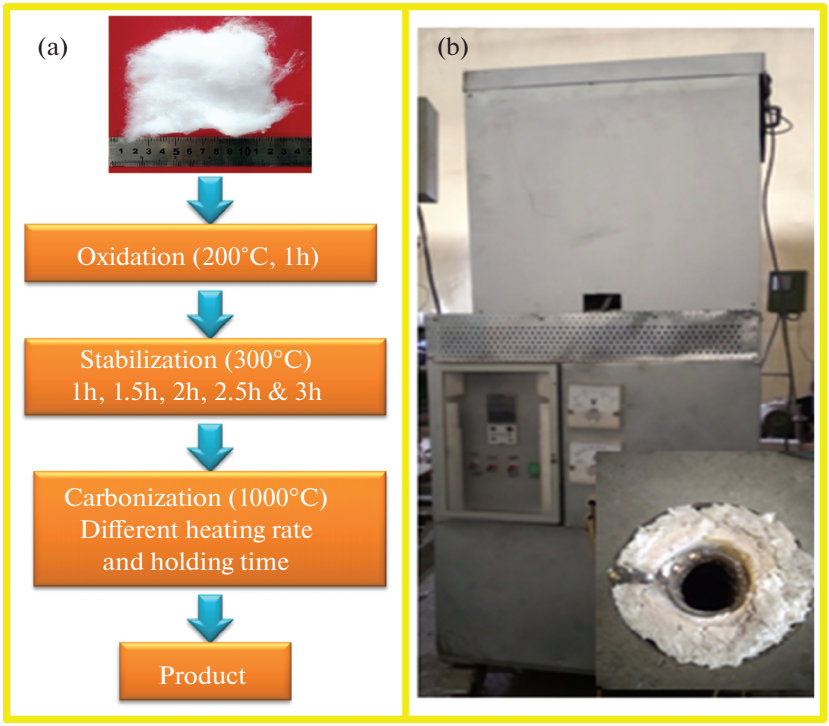

Fig. 1. The schematic of the preparation of CFs from (a) and A LDT 1280 resistive vertical furnace used for the preparation of CFs from cotton (b). Inset represents the cross-section of the furnace.

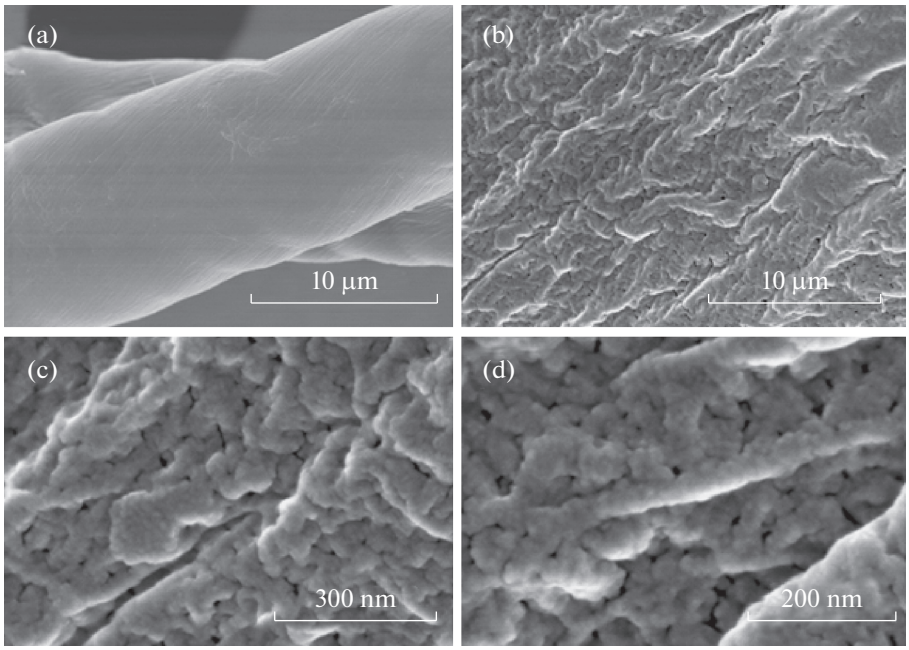

Fig. 2. SEM images of cotton precursor at different magnification 10 (a), 1 μm (b), 300 (c) and 200 nm (d).

fewer physical defects. A good carbon fiber precursor should have the characteristics like a round cross-section, fine denier, high strength, and modulus [12]. SEM image revealed cotton precursor collected from Northern Vietnam can a good source for the preparation of carbon fibers.

Figure 3 shows the X-ray diffraction patterns of cotton fibers stabilized at 300°C with different annealing times such as 1, 1.5, 2, 2.5, and 3 h. The structural transformation of cotton is very complicated because there are H and OH atoms in the lattice nodes. Therefore, in principle, the longer the time, the more H sep-

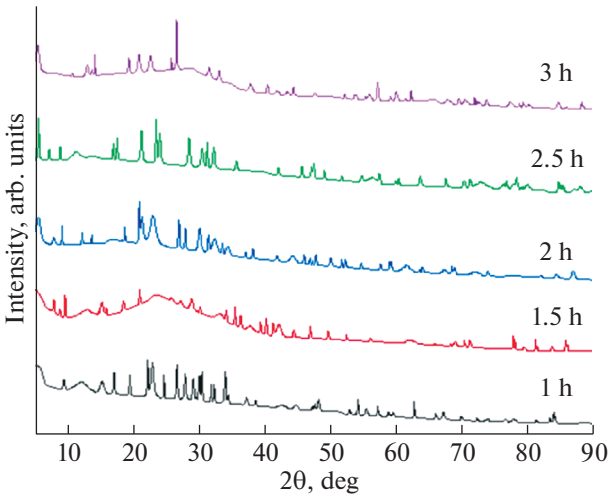

Fig. 3. X-ray diffraction patterns of natural cotton samples collected from Northern Vietnam stabilized at 300°C.

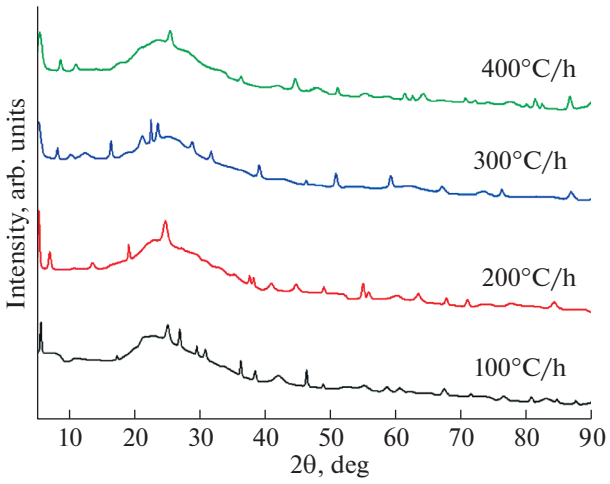

Fig. 4. X-ray diffraction patterns of cotton carbonized at 1000°C for 1h with different heating rates.

arates from the cotton [12, 15, 16]. It is noted that a lot of crystalline peaks appeared in the XRD pattern of all samples. However, it is very hard to identify the precise phase of the peaks that emerged in the XRD of cotton fibers stabilized at 300°C with different annealing times.

We have carried out the carbonization of cotton in an inert gas atmosphere to a temperature of 1000°C with the heating rate of 100, 200, 300, and 400°C/h, respectively. The XRD pattern of all samples carbonized at 1000°C with different heating rates shows the amorphous hump around $2\theta = 23°$ along with some unknown crystalline peaks which is the sign of formation of CFs. Figure 4 indicates that 400°C/h is better to form CFs. Hence, the sample obtained by carbonization at 1000°C with 400°C/h was further annealed at 2, 3, and 4 h. XRD patterns of CF-3 prepared from cotton with the heating rate of 400°C/h with different annealing times at 1000°C are shown in Fig. 5. The XRD pattern of all the three samples exhibits two crystalline peaks at $2\theta = 25°$, and 44°, which correspond to the (002), and (100) planes of crystalized CFs, respectively. This result is well-matched with the literature [14–16]. All CF-3 fibers have the same crystallinity. Broad diffraction found in the XRD pattern of all CFs samples indicated that the prepared products have nanocrystalline characteristics and it confirmed the natural cotton fibers of Northern Vietnam were converted to the carbon crystal lattice.

Figure 6 shows the optical images of the CFs obtained by carbonization conditions at different heating rates. It clearly shows the morphological characteristics and shape of the CFs. It is noted that fiber thickness was around 3–15 μm irrespective of heating rates. Figures 7–10 revealed the structure of CF-3 with the different heating rates which shows that the morphology of CF-3 prepared with different heating rates was different. From Figs. 7, 8, CF-3 consists of spheres with sizes from 50 to 80 nanometers was formed at low heating rates (with a heating rate of 100 to 200°C/h). When increasing the heating rate to 300 and 400°C/h, the CF-3 with fiber-like morphology was formed. It is clear that with a low heat-up rate, the H and OH atoms gradually separate from the lattice sites and crystallize as spherical nanoparticles. As the heating rate increases, the H and OH atoms separated from the lattice node of the cotton lattice rapidly leads to the fibrous growth of carbon crystal lattice.

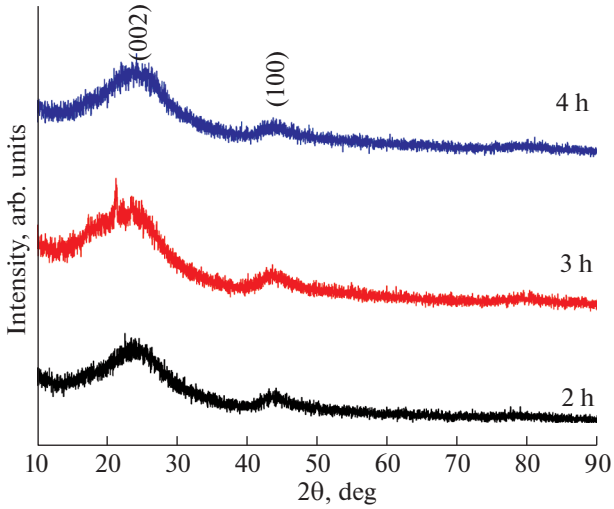

Fig. 5. X-ray diffraction patterns of CF-3 prepared from cotton with the heating rate of 400°C/h with different annealing time at 1000°C.

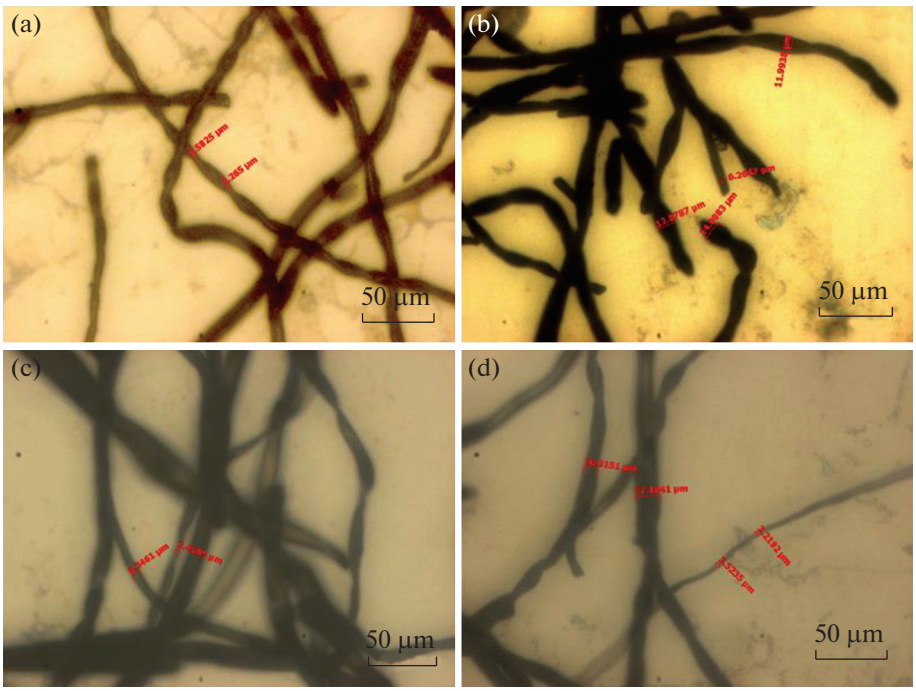

Fig. 6. The optical images of the CFs obtained by carbonization condition at different heating rates.

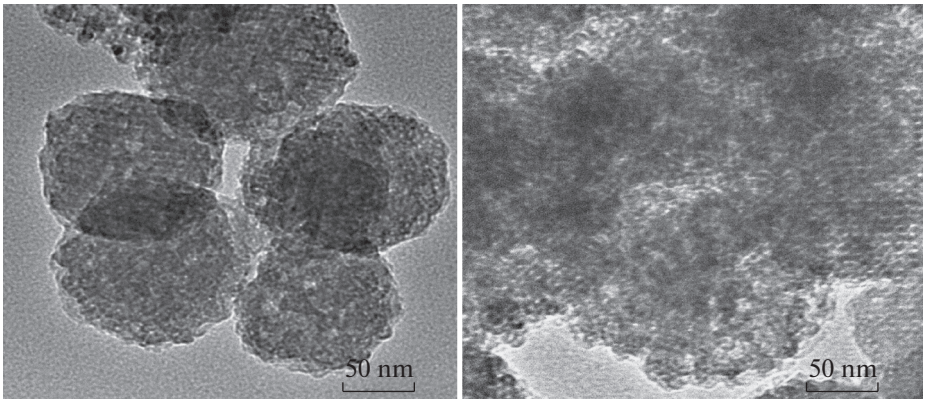

Fig. 7. TEM image of CF-3 fiber with the heating rate at 100°C/h. T_{max} =1000°C.

The carbon structure and content of CF material provide adequate thermal protection at extremely high temperatures [21–23]. The choice of insulating material is critical when temperatures exceed 1000°C. At this time, the cost-performance factor leads to carbon-based insulating materials. Insulation materials based on carbonized and graphitized CFs derived from renewable sources may provide a cost-effective solution [27]. Controlling the carbon yield and thermal conductivity of cellulose-derived carbon fibers by pyrolyzing the precursor fibers at appropriate temperatures could be a simple strategy with real implications on the prospective and economic viability of CFs derived from renewables for desired applications. Because of their poor thermal conductivity, carbon-based insulations excel radiation shields in high-temperature applications [23].

Figure 11 shows the calculated thermal conductivity at room temperatures $T = 25$°C for cotton precursor and CFs obtained by carbonization condition at different heating rates. Table 1 shows the value of thermal conductivity for cotton precursor and CFs obtained by carbonization conditions at different heating rates. The carbonization process leads to a significant decrease in the value of the thermal conductivity of the initial cellulose fiber, respectively, to an

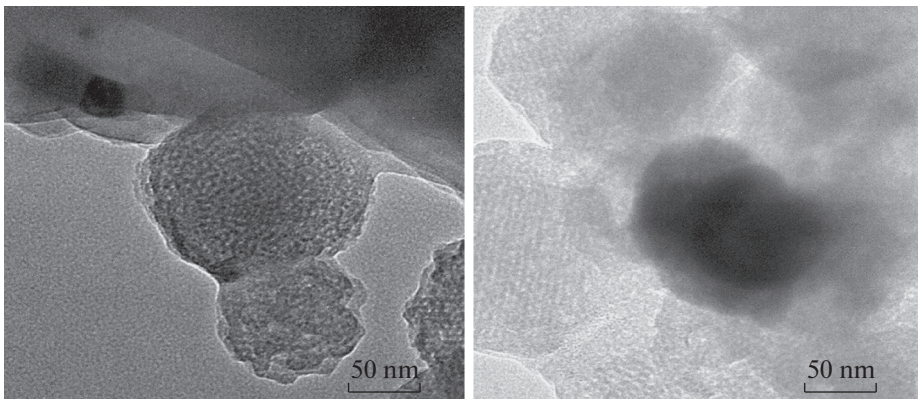

Fig. 8. TEM image of CF-3 fiber with the heating rate at 200°C/h. T_{max} =1000°C.

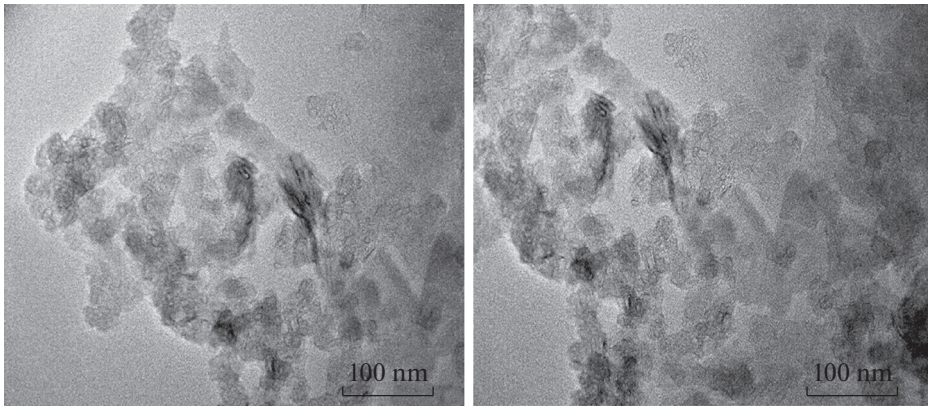

Fig. 9. TEM image of CF-3 fiber with the heating rate at 300°C/h. T_{max} =1000°C.

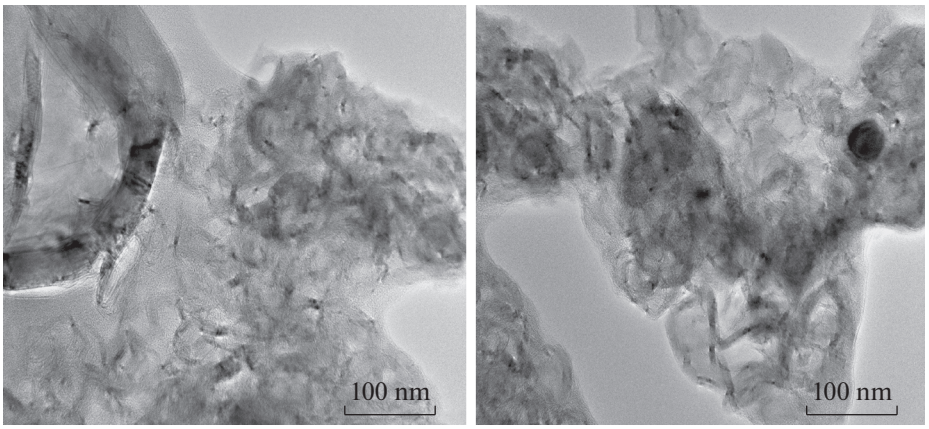

Fig. 10. TEM image of CF-3 fiber with the heating rate at 400°C/h. T_{max} = 1000°C.

increase in their thermal insulation capacity. It is shown that the heating rate during the carbonization process affects the values of the thermal conductivity coefficient λ of the obtained SF-3 carbon fibers. Nevertheless, the results of measuring λ values revealed that an increase in the heating rate during the carbonization process leads to a certain decrease in the value of the thermal conductivity of carbon fibers, making them more heat-insulating. This can be explained by the fact that a high heating rate contributes to the massive release of groups of H, O atoms, as well as carbon atoms from initial cellulose fiber, which leads to the

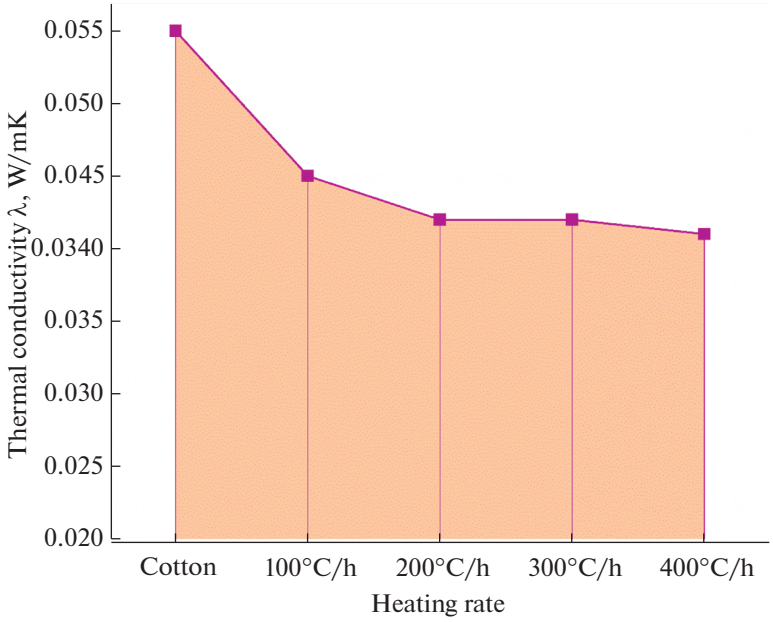

Fig. 11. The calculated thermal conductivity at room temperatures $T = 25°C$ for cotton precursor and CFs obtained by carbonization at different heating rates.

formation of a large number of pores inside the obtained carbon fibers, that is, makes the product of the carbonization process more porous (see Figs. 9, 10), respectively, more heat-insulating. Thus, carbon fibers obtained at a heating rate of 400°C/h are most suitable for the manufacture of thermal insulation materials.

The composite sample is made from CF-3 carbon fiber and tested for thermal conductivity at 200°C according to the ASTM-C177 standard. The measured thermal conductivity at 200°C is $\lambda = 0.057$ W/mK which is rather lower than aluminum oxide, which is often used as an insulating material in high-temperature technology [28–30]. It revealed that prepared CF-3 can be a potential material for making outer ring insulation in high-temperature furnace environments.

Table 1. The thermal conductivity of cotton precursor and CFs obtained by carbonization condition at different heating rates

Sample	Sample, °C/h	Thermal conductivity λ (W/mK) at room temperatures $T = 25°C$
1	Initial cotton fibers	0.055
2	100	0.045
3	200	0.042
4	300	0.042
5	400	0.041

CONCLUSIONS

From the technological modes for producing type III carbon fiber surveyed in this article and concluded the production technology parameters of CF-3 from the precursor fibers of cotton in Northern Vietnam. The optimized parameters are heating rate 400°C/h; annealing time 2 h; carbonization temperature 1000°C and N_2 as protective gas. Thermal conductivity studies revealed that prepared CF-3 using the above-optimized parameters can be a potential material for making outer ring insulation in high-temperature furnace environments. Pyrolyzing the precursor fibers at appropriate temperatures to control the properties and thermal conductivity of cellulose-derived carbon fibers might be a simple method with major effects on the potential and economic feasibility of CFs produced from renewables for desired applications.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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