

Article

Thermal Characteristics of Okra (*Abelmoschus Esculentus*) Fibers Obtained via Water- and Dew-Retting

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In Memory of Dr Eng. Agnieszka Komisarczyk

Featured Application: Fibrous composites can be used in different industries, such as: the aerospace industry, automotive industry, as well as in medical equipment, building elements, ship, yacht and boat construction applications, wind energy devices, pressure vessels, satellite antennas, different sports equipment, etc. The one of most interesting applications of fibrous composites concern the aerospace industry. The aircraft structure - both military and civilian - is forcing their manufacturers to search for innovative materials that reduce weight, maximize effective fuel consumption and maintain aerodynamic balance. Composites made from lightweight construction materials are especially applied for more durable materials useful in special constructions, because they are lighter than previously used, relatively easy to get, and they are resistant to high temperatures.

Abstract: In this study, fibers were extracted from different parts of the okra plant (*Abelmoschus esculentus*) via water- and dew-retting methods. The fibers were subjected to physical and thermal analyses. The fibers obtained from the upper part of the okra plant show higher breaking strength and lower linear density. Fibers obtained via water-retting exhibited higher breaking strength, elongation at break rates, and lower linear density values. The paper also presents the results of thermogravimetric analysis of the okra fibers. Tests were carried out in oxygen and inert gas atmospheres. The temperature range of the main thermal decomposition stage was in the 275–400°C for range thermo-oxidation and 300–425°C for pyrolysis investigation. Slight differences were found in the thermal resistances of the tested fibers, which was confirmed by an analysis using the α_s - α_r methodology. The calculated activation energy values show a large-spread range.

Keywords: okra bast fibers; agro-residual fibers; thermal properties; mechanical properties

1. Introduction

The introduction should briefly place the study in a broad context and highlight why it is important. It should define the purpose of the work and its significance. The current state of the research field should be reviewed carefully and key publications cited. Please highlight controversial and diverging hypotheses when necessary. Finally, briefly mention the main aim of the work and highlight the principal conclusions. As far as possible, please keep the introduction comprehensible to scientists outside your particular field of research. References should be

numbered in order of appearance and indicated by a numeral or numerals in square brackets, e.g., [1] or [2,3], or [4–6]. See the end of the document for further details on references.

Sustainable development (SD) is defined by the World Commission on Environment and Development as:

"development that meets the needs of the present without compromising the ability of future generations to meet their own needs",

in the book "Our Common Future", more famously known as the Brundtland Report [1]. One way to implement the principles of sustainable development is to reduce the use of non-renewable resources on a scale that allows them to be gradually replaced by appropriate substitutes with a renewable origin. Environmental protection is gradually enforced by both ever-tightening EU legal regulations that limit and even eliminate the use of many existing technologies and materials in conventional industrial production and by the increase in societal environmental awareness. That is why the search for improving eco-friendly production methods and inventing novel ones and the interest using new material solutions, with particular emphasis on materials based on renewable sources, has become one of the most important tasks for science and technology today [2,3].

Currently, as the world is struggling with growing waste problems, new legal regulations are being introduced to guarantee the production of more environmentally-friendly materials. They promote new products that can be recycled or are naturally biodegradable. An important argument is the possibility of much easier subsequent thermal utilization by burning them for energy recovery. All these criteria are met by biocomposites, i.e. materials in which at least one component is of natural origin [4].

Composite materials have been known to people for thousands of years. Historical data shows examples of the use of composites as early as the 5th century BC [5]. Currently, their use is very common and shows a consistently increasing trend. A composite consists of at least two components with different properties. As one of the components, fibers are often used to strengthen the material. In particular natural fibers, including cellulose fibers, play an important role in this type of composite [3].

The development of contemporary environment-friendly composite materials is associated with both the constant search and development of technologies for obtaining the composites themselves and the use of natural plant fibers. The interest and selection of natural fillers as additives in composite materials are associated with the current tendency of many industries to recycle plastics, reduce manufacturing costs and control the product life cycle through using environmentally-friendly materials [6]. Composites reinforced with natural fibers are an attractive alternative to glass- and synthetic fibers due to their biodegradability, low price, and relatively easy local availability with still good mechanical parameters. The introduction of microbiologically degradable plant fibers into biostable polymers may accelerate their degradation and thus have a significant impact on waste management and environmental protection. In the near future, it may turn out that polymer composites with natural fibers will find application in many areas of our lives. They are already used for product components in the automotive, electromechanical, and aviation industries. It is expected that 20 to 30% of the global production of glass fiber products will soon be replaced with composites based on natural fibers.

Several methods are used to obtain natural plant fibers, including water-retting, dew-retting, chemical-retting, and mechanical decortication [3]. Among those methods, water-retting and dew-retting have been applied traditionally. Dew-retting is thought to be the oldest retting

technique. In this technique, plant stems are laid on the ground under a thin layer of soil and kept there for three to four weeks. Plant stems are immersed in water tanks for the water-retting method. The properties of dew-retted fibers were reported to be inferior and show higher variability compared to water-retted fibers. However, dew-retting has still some advantages, such as ease, low cost, and less environmental impact compared to water retting [7].

Among plant fibers, cotton [8], flax [9], hemp [10], jute [11], and sisal [12] should be distinguished for attracting research and commercial interest for use in composites over the last few decades. However, several different plant varieties planted mainly for supplying the food industry may be evaluated as alternative fiber sources [13]. Unused parts of different edible plants, including okra stems and branches [14], wheat straw [15], nettle stems [16], corn husks [17], and banana pseudo-stems [18], can be used as sources of fiber for composite reinforcement applications. By utilizing agricultural residues for fiber production, not only will the environment be saved due to using biodegradable materials based on renewable sources, but also developing rural communities will prosper as their crops receive added value. Furthermore, more arable land may be allotted for food production to feed our growing world population [19].

Okra (*Abelmoschus esculentus*) is a plant grown in tropical and subtropical regions, mainly for eatable fruits and for its gum, to serve the pharmaceutical industry [14,20]. The first written mention of okra dates from 1216 and concerns Egyptian crops. The domesticated form of the species *Abelmoschus esculentus* spread further to the regions of the Red Sea and the Arabian Peninsula, and then also to Southern Europe. In the eighteenth century, okra also appeared in the English dictionary, and slaves brought it from Africa to the United States. Today, other than Africa, the okra plant is successfully grown in the southern part of the USA, the Caribbean, South America, the Middle East, Greece, and Turkey. Nevertheless, the okra plant is generally produced by underdeveloped countries across the globe. According to the Factfish database, total okra production was almost 10 million tons in 2017. That year, the top three okra producers were India, Nigeria, and Sudan. More than half of the ten greatest okra producers were African countries [21].

The main application of okra is food; however, the remaining fragments of the plant can be used as a structural element in composite materials. Okra bast fibers can be considered as an alternative to the most commonly used fibers, such as jute, flax, or hemp. This is in accordance with the general trend of trying to broaden the number of botanical species from which fibers are extracted [22,23].

An additional advantage of using okra bast fibers is the fact that its inedible parts are used, which are normally recyclable waste. Obtaining okra stalk fibers is, in fact, removing food production waste from the fields. Okra fiber production is not in competition with food production, both processes take place in parallel in the same area [24].

Bark from the okra plant can be utilized as a source of natural fibers. Fibers can be obtained from okra plant bark, similar to other conventional plant fibers, using various methods, including water-retting, dew-retting, chemical-retting and mechanical extraction by a number of degumming techniques based on the biological activity of microorganisms, and the effects of chemical agents or mechanical means [3,24].

Okra bast fibers are technical fibers. Hence, they are not single-cell elementary fibers like cotton fibers. They are multicellular lignocellulosic fibers similar to jute and hemp. Okra bast fibers are partially separated bundles of cellulosic fibers attached by hemicellulose, lignin, and pectin [19,25].

The literature on okra bast fibers is limited to a few studies. The influence of some chemical treatments on the physical characteristics of okra bast fibers was investigated by Khan et al. [26]. The mechanical, chemical, morphological, and thermal performance of okra bast fibers and the effects of some chemical treatments, including scouring, bleaching, and acetylation, on these were studied by De Rosa et al. [22,27]. Yilmaz et al. [14] investigated the influence of some chemical and enzymatic treatments on the physical, mechanical, and chemical characteristics of okra bast fibers. They also dyed the okra fibers with an industrial biowaste colorant (green mate waste) and studied the performance of okra fibers in removing heavy metal ions from aqueous solutions.

Alam and Khan [28] reported the chemical composition of okra bast fibers as cellulose (60–74%), hemicelluloses (15–20%), lignin (5–10%), and pectin and waxes.

Even though the literature contains some work on okra bast fibers, no study on dew-retting okra bast fibers is present, as all of the mentioned studies investigate water-retted okra bast fibers. Furthermore, a systematic study of the thermal properties of okra bast fibers is also not present.

The aim of this work is to investigate and compare the properties of okra fibers obtained from various parts of the plant via dew-retting and water-retting. Special emphasis has been paid to the thermal performance of okra bast fibers as they are processed under various conditions as part of composite systems operating at elevated temperatures. Therefore, thorough knowledge of their thermal behavior is of utmost importance.

2. Materials and Methods

Materials and Methods should be described with sufficient details to allow others to replicate and build on published results. Please note that publication of your manuscript implicates that you must make all materials, data, computer code, and protocols associated with the publication available to readers. Please disclose at the submission stage any restrictions on the availability of materials or information. New methods and protocols should be described in detail while well-established methods can be briefly described and appropriately cited.

Research manuscripts reporting large datasets that are deposited in a publicly available database should specify where the data have been deposited and provide the relevant accession numbers. If the accession numbers have not yet been obtained at the time of submission, please state that they will be provided during review. They must be provided prior to publication.

Interventionary studies involving animals or humans, and other studies require ethical approval must list the authority that provided approval and the corresponding ethical approval code.

2.1. Materials

Okra (*Abelmoschus esculentus*) stems were collected from local agricultural farms in Denizli providence, Turkey. All chemicals employed were analytical reagent grade from Sigma-Aldrich.

2.2. Methods

2.2.1. Fiber preparation methodology

Before starting any degumming procedures, the okra plant stems were divided into three as the top, middle, and bottom portions of them were separately subjected to retting processes.

2.2.2. Water-retting method

Water-retting was carried out at room temperature ($20 \pm 3^\circ\text{C}$) for around 30 days by immersing okra stems in closed beakers filled with tap water.

2.2.3. Dew-retting method

Dew-retting was carried out at room temperature (average 20°C) for around 15 days by burying okra stems in a tray filled with soil.

2.2.4. Linear density measurements

All experiments were made under specified climate conditions, as described in EN ISO 139:2006 standard with annex A:2011. The standardized conditions were as follows: Air temperature: $20 \pm 2^\circ\text{C}$ and humidity: $65 \pm 4\%$. Linear density was measured as described in PN-EN 13392:2002. 50 specimens of each sample were measured.

2.2.5. Mechanical properties measurements

Samples were tested using a Zwick ZW2.5/TNIP apparatus, according to the conditions described in PN-EN ISO 2062:2010 standard. Briefly, fiber length: 500 mm, speed: 500 mm/min, pressure: 0.5 ± 0.1 cN/tex. 50 specimens of each sample were measured. The results of the linear density and mechanical measurements were statistically investigated by applying analysis of variance with α at the 0.05 significance level.

2.2.6. Thermogravimetric analysis

The thermal stability of the okra fibers was investigated by thermogravimetric (TG) analysis using a Perkin Elmer TGA 7 instrument. The measurements were conducted at a $10^\circ\text{C}/\text{min}$ heating rate (platinum pan) in dynamic air and nitrogen atmospheres (the gas flow rate for both gases was $20 \text{ cm}^3/\text{min}$). The weight of each sample was about 7 mg. All measurements were repeated at least four times.

2.2.7. Differential Scanning Calorimetry

To characterize their differential scanning calorimetry (DSC), okra bast fibers were investigated using a Q2000 TA Instrument Inc. calorimeter. The heat was increased stepwise at $10^\circ\text{C}/\text{min}$. The material was cyclically heated to 300°C .

3. Results

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation as well as the experimental conclusions that can be drawn.

The okra fibers were obtained from various parts of the plant via water-retting and dew-retting procedures. Depending on the origin of the fiber and the way it was processed, the samples were identified by the following symbols (Table 1):

Table 1. Sample codes.

Sample source	Sample code
Water retted bottom okra bast fibre	BBW
Water retted middle okra bast fibre	MBW
Water retted upper okra bast fibre	UBW
Dew retted bottom okra bast fibre	BBD
Dew retted middle okra bast fibre	MBD
Dew retted upper okra bast fibre	UBD

3.1. Fiber yield

Fiber yield is the weight of fibers obtained per unit weight of okra stem in percentages. The fiber yield rates varied between 10.85 and 14.73% for the studied okra bast fibers. Stated in other

words, to produce 1 g fiber, 6.92–9.22 g of okra stem should be retted. No significant effect of the okra plant portion or retting method was detected (p values 0.63 and 0.76, respectively)(Table 2).

Table 2. The effect of plant part of extraction and retting method on physical and mechanical properties of okra bast fibers

Okra bast fiber	Fiber yield [%]	Linear density [tex]		Breaking strength [cN/tex]		Elongation at break [%]	
		μ	σ	μ	σ	μ	σ
BBW	14.47	11.90	4.30	42.01	17.40	3.33	1.07
MBW	14.33	10.25	2.66	45.76	16.29	3.40	0.92
UBW	12.65	9.45	2.79	51.80	18.30	3.48	1.30
BBD	14.73	17.09	6.95	33.93	18.99	2.75	0.98
MBD	10.85	13.13	3.68	32.50	14.09	2.83	0.87
UBD	14.25	11.17	3.07	37.12	16.71	2.90	0.89

3.2. Linear density of fibers

The linear densities values of okra bast fibers are presented in Table 2 and Figure 1. As seen, the linear density results show the trend bottom>middle>top (p-value 3.69×10^{-11}). This trend is valid for both water-retted and dew-retted fibers. Similar findings were reported by Yilmaz et al [14] for okra bast fibers and by Bacci et al [16] for nettle fibers. These findings hint that okra bast fibers, which lie throughout the okra stem, show a tapered shape. However, it should also be taken into consideration that the measured fibers are not single fibers; they are a bunch of fibers in reality. So fiber separation- and extra-cellulosic substance removal efficiencies also play an important role in the final linear density of the fibers. The dew-retted fibers generally exhibited higher linear density values compared to water-retted ones (p-value 7.29×10^{-11}). Longer durations of dew retting may be tested if it leads to lower linear density values. Histograms of different samples are shown in Figure 2. The broadest diameter distributions belong to fibers extracted from the bottom portion okra stems for both water- and dew-retting.

Linear density values of the obtained okra bast fibers are given in Figure 1.

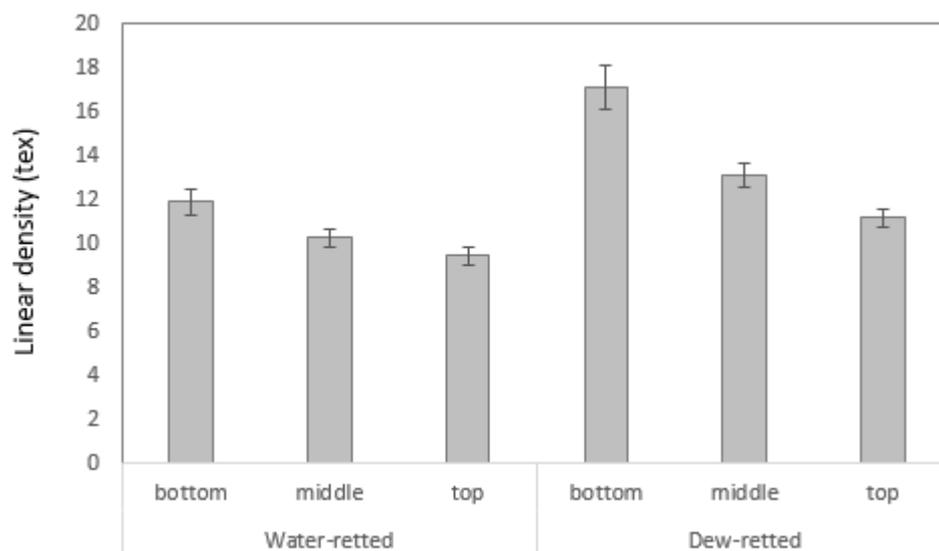


Figure 1. Effect of plant section of fiber extraction and the retting method applied on fiber linear density (tex). (Error bars represent standard errors.)

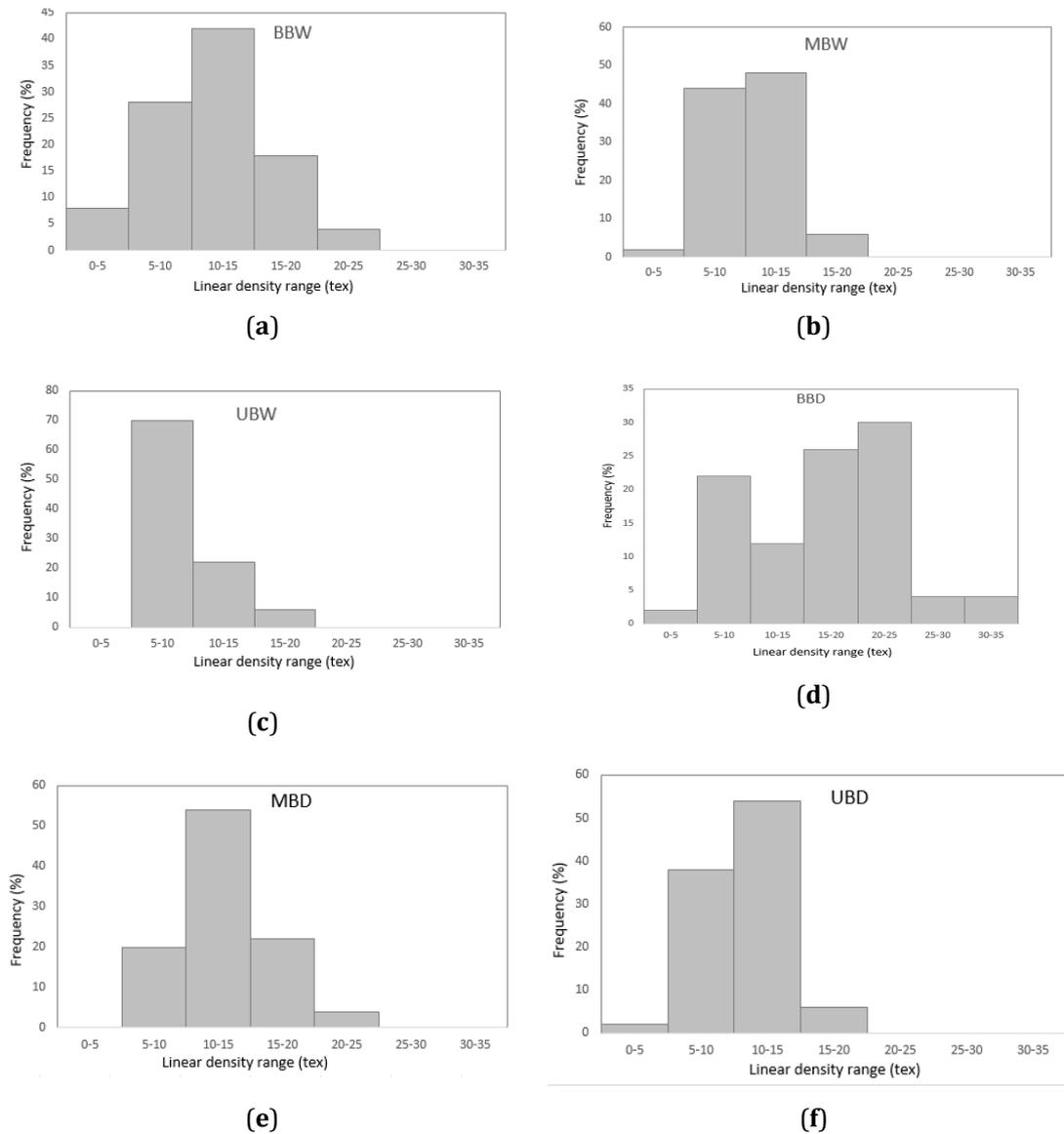


Figure 2. Linear density histograms of (a) BBW, (b) MBW, (c) UBW, (d) BBD, (e) MBW and (f) UBD fibers.

3.3. Mechanical properties

Because the important role of the fibrous component in composite materials is to transfer mechanical load, it is necessary to determine the basic mechanical properties of the obtained fibers. Table 2 and Figures 3 and 4 show the results of the breaking strength and elongation at break measurements for the tested fibers.

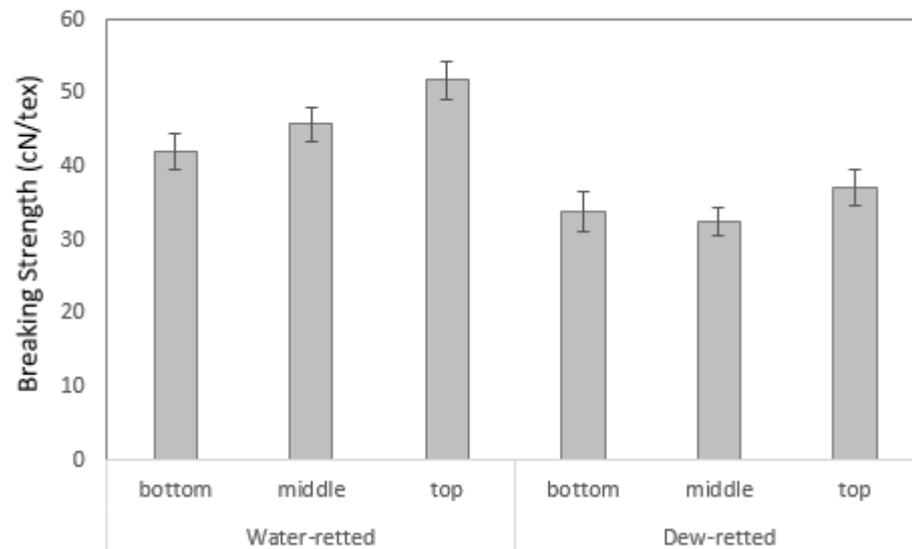


Figure 3. Effect of plant section of fiber extraction and the retting method applied on fiber breaking strength (cN/tex). (Error bars represent standard errors.)

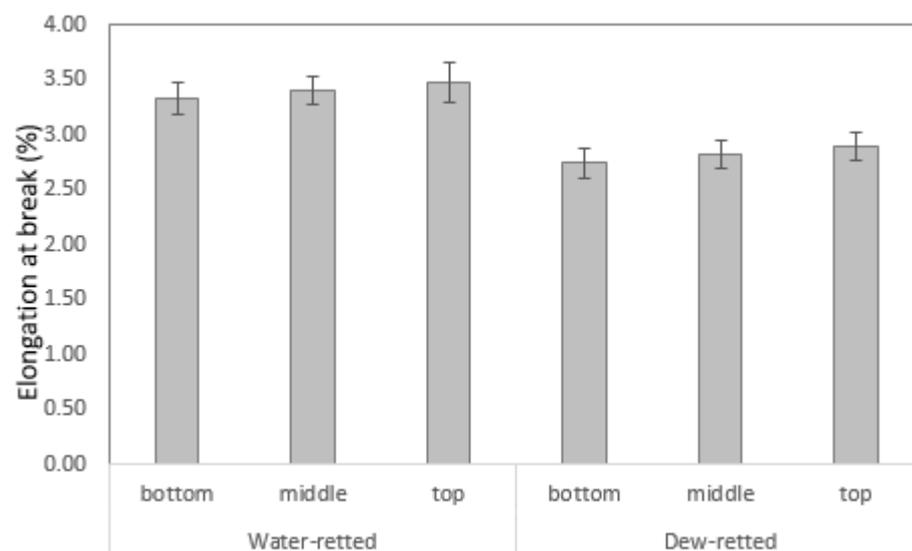


Figure 4. Effect of plant section of fiber extraction and the retting method applied on fiber elongation at break rates (%). (Error bars represent standard errors.)

Both plant fraction and retting method were found to affect breaking strength (p values 0.02 and 3.24×10^{-9} , respectively). The greatest breaking strength (51.80 cN/tex) was obtained from the fibers extracted from the upper part of the okra stem via water retting. The breaking strength values vary between 42.01–51.80 cN/tex for the water-retted fibers and 32.50–37.12 cN/tex for the dew-retted fibers. In terms of elongation at break rates, while no significant effect of extraction fraction was found, the retting method had a significant effect (p values 0.57 and 1.24×10^{-6} , respectively). The water-retted fibers exhibit higher elongation at break rates (3.33–3.48%) compared to the dew-retted ones (2.75–2.90%). The attained results agree with the literature, which reports a lower performance of dew-retted fibers compared to water-retted fibers [7].

3.4. Thermal properties

Highly heat-resistant composite materials are traditionally used for applications such as automotive components, highly loaded plain bearings, gears, rings, fittings in the chemical industry, elements sterilized by steam, ethylene oxide and gamma radiation, pumps, gears, or components. Most often, such materials are reinforced with glass or carbon fibers. Composites reinforced with okra fibers, of course, cannot be counted among the materials used in high-temperature applications. However, performing full thermal degradation characteristics will allow both accurately describing and learning about this process, as well as determining the boundary conditions that determine the range of practical applications for these fibers and composites.

3.4.1. Thermo-oxidation

Small sample weight change methods have long held an important place among techniques commonly used in evaluating and investigating polymeric materials. They are a means of assessing thermal stability preliminarily, but they also serve as the backbone of many kinetic studies, some of which have strongly influenced the growth of polymer science. It must always be born in mind, however, that such empirically determined decomposition temperatures are highly specific since their measured values depend on procedural variables and superficial decomposition criteria.

If the thermal decomposition process is carried out in an atmosphere containing oxygen, then we are dealing with thermo-oxidation, an oxidation process caused by thermal energy. Compared to thermal decomposition in an inert atmosphere, the nature of the TG curve, the characteristic temperatures, and the type of processes are different, which is manifested in other volatile decay products.

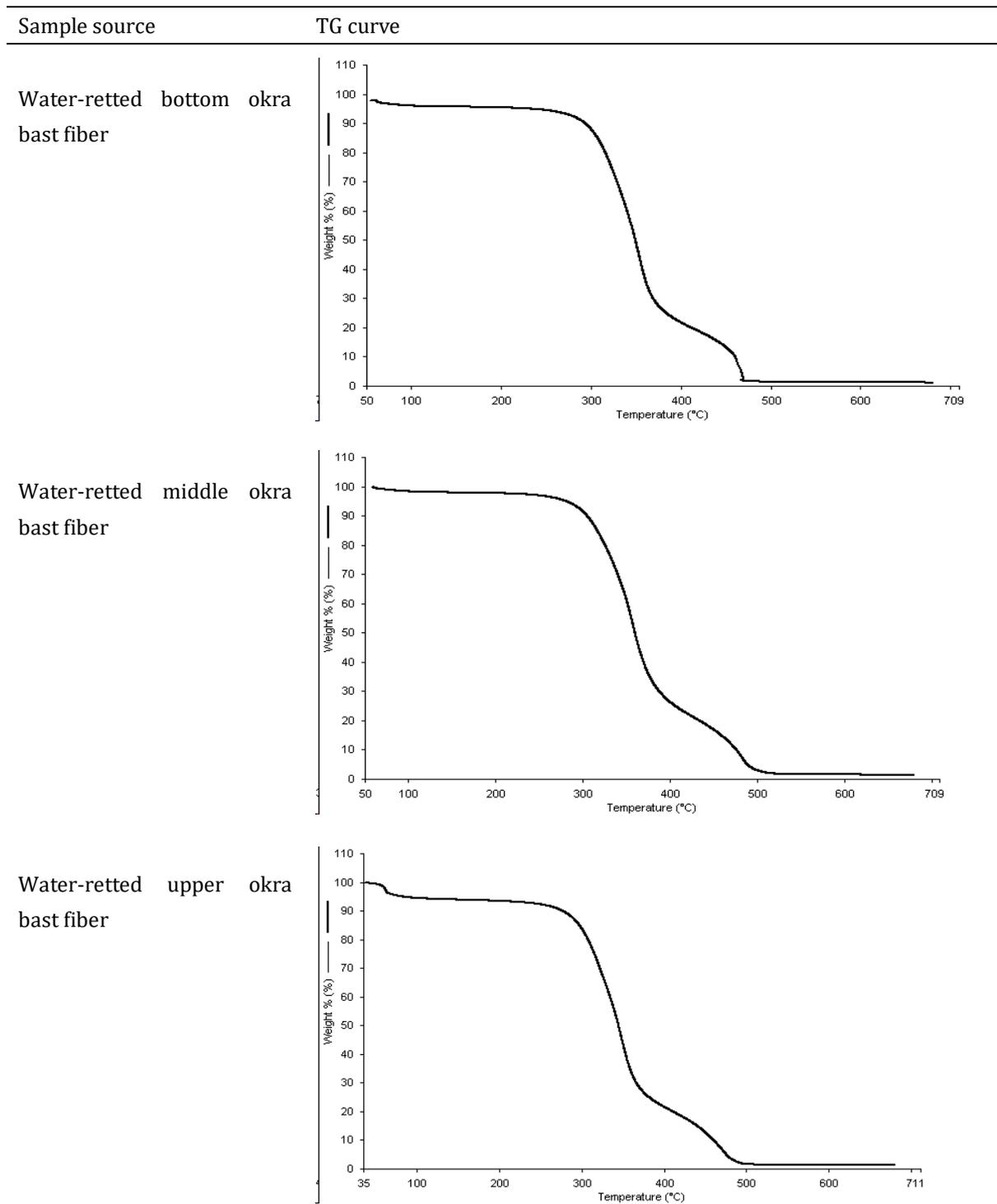
Full thermal analysis requires testing in both a reactive and inert atmosphere, as well as at different heating rates. Changing this parameter causes a shift in the thermogravimetric curve—the faster heating rate is characterized by the subsequent occurrence of individual decomposition stages. This significantly affects the kinetic characteristics of the process.

Because understanding the dependence between thermal resistance and the chemical composition of compounds used in high temperatures is essential, it is important to determine the thermal decomposition parameters, such as activation energy (E), reaction order (n), or frequency coefficient (A). These parameters are of vital importance for determining the polymer degradation mechanism [29,30] [4,5] and its thermal stability [6].

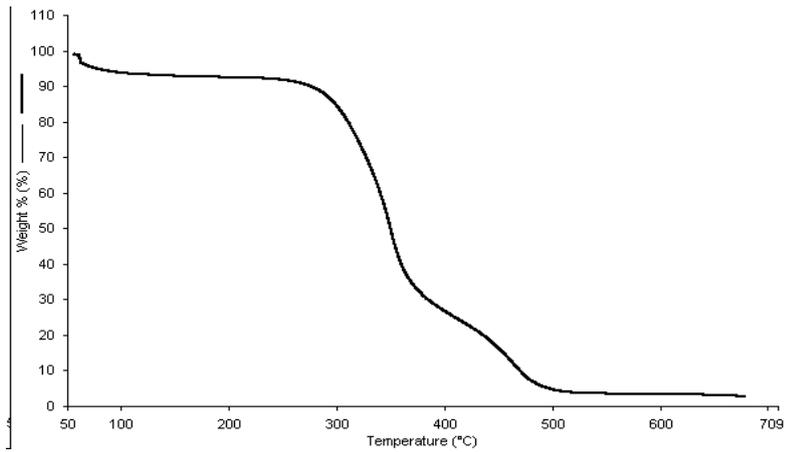
There are a number of methods used to determine the kinetic pyrolysis parameters. They vary not only in the kind of data analysis and assumed hypotheses but also in the method of mathematical elaboration. However, even the most modern methods using complicated calculation schemes make use of the original basic theories [31–35].

In the presented work, two methods were selected for kinetic analysis, differing in theoretical approach in terms of assumptions and simplifications. The most popular approximations to the Arrhenius integral in polymer science are those of van Krevelen [36] and Coats and Redfern [37].

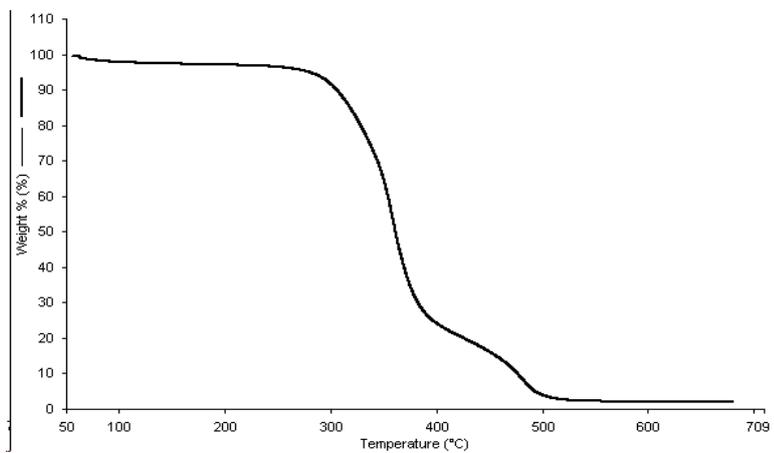
Tables 3 and 4 respectively show examples of thermogravimetric curves for the distribution of samples tested under thermo-oxidation conditions and characteristic temperatures for thermal decomposition.

Table 3. Representative TG curves of analyzed samples in thermooxidative conditions.

Dew-retted bottom okra bast fiber



Dew-retted middle okra bast fiber



Dew-retted upper okra bast fiber

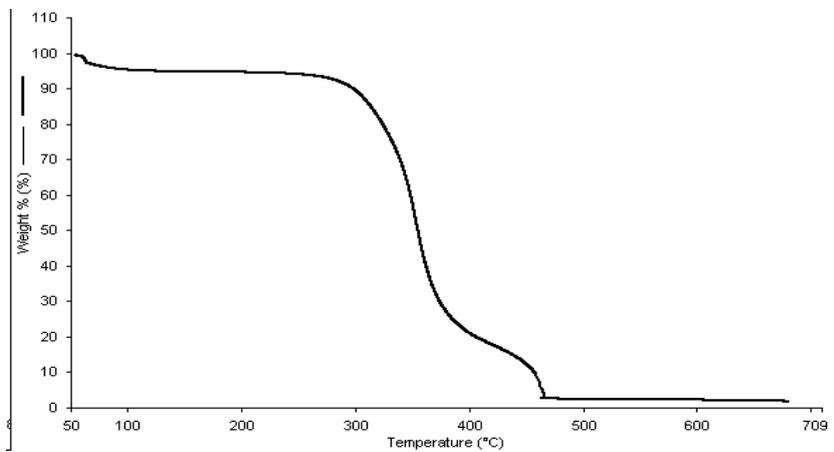


Table 4. Characteristic temperatures (average values) of main stage thermal degradation of analyzed samples.

Sample	T _{intit}	T _{50%}	T _{final}
BBW	291.4	355.0	382.8
MBW	287.4	366.1	398.0
UBW	275.8	342.4	375.5
BBD	281.6	354.3	383.5
MBD	298.4	370.2	397.9
UBD	298.6	353.7	397.7

As can be seen from the data presented in Tables 3 and 4, the thermal distribution curves of the samples have a two-stage character. The first stage is related to depolymerization and thermal degradation of cellulose macromolecules. In the second, afterburning of low-molecular products of the first stage takes place. The temperatures characteristic of the first, main stage of decomposition are shown in Table 4. The distributions of fibers from different parts of the plant are similar in nature and occur in similar temperature ranges. For the okra bast fibers, the temperature range of thermal characteristics is about 20°C—the start of decomposition is 275–298, T_{50%} is 342–371 and the end of the process is 375–399°C. The thermal degradation of fibers obtained by the water-retting method occurs slightly earlier (T_{50%} = 354.5°C) than those from the dew-retting technique (T_{50%} = 359.4°C).

The processes of the thermal degradation of okra fibers were compared using the α_s – α_r evaluation method [38,39], which compares the thermal reactivity of different substances on the comparison base. The data obtained from the TG of water-retted bottom okra bast fiber (BBW) were used as the reference base and denoted by α_r , whereas the other five by α_s . The α coefficient was determined using the following equation:

$$\alpha = (w_i - w) / (w_i - w_f), \quad (1)$$

where:

- w is the mass fraction of a substance at a given temperature,
- w_i is the mass fraction of the substance at the initial temperature and
- w_f is the mass fraction of the substance at the final temperature

The plots of α_s vs. α_r (Figure 5) were prepared for the main transformation range of a TG run. As one can see in Figure 5, dew-retted middle okra bast fiber (MBD) has slightly higher thermal stability than the reference sample, whereas the other samples are less stable. The sample of UBW (water-retted upper okra bast fiber) is the least stable. A similar conclusion can be drawn from the α_s coefficient temperature plot (Figure 6). TG measurements show that from the point of view of their thermal stability, the investigated fibers can be ranged as follows: MBD > MBW > UBD > BBD > BBW > UBW. As can be seen in Figures 5 and 6, this order does not change throughout the whole course of the main thermal degradation stage, which leads to the conclusion that fibers coming from the middle part of okra bast plant are, very slightly, better in thermal stability than those coming from other parts.

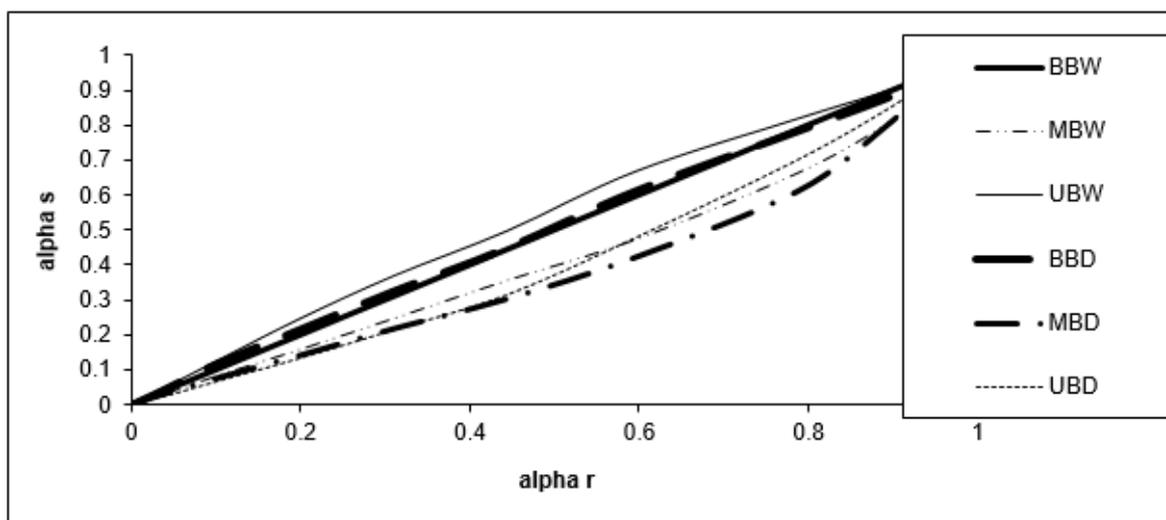


Figure 5. Alpha s – alpha r dependence of okra bast fibers.

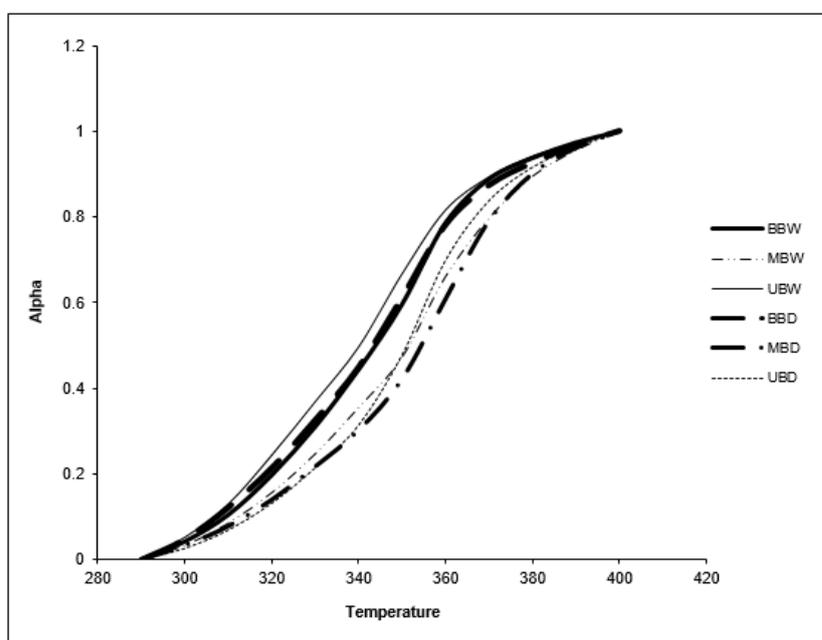


Figure 6. Alpha vs. temperature relationship for okra bast fibers.

The main stage of thermal decomposition under thermo-oxidation conditions was subjected to kinetic analysis. The activation energy values of the decomposition process were calculated using the Coats-Redfern method [37]. The results of the analysis are shown in Table 5.

Table 5. Activation energy of thermooxidation process of okra fibers (standard deviation 5%).

Sample	Activation energy [kJ/mol]
BBW	84.1
MBW	69.9
UBW	41.9
BBD	46.6
MBD	36.4
UBD	39.3

Based on the data from Table 5, the EA values at the given conditions (kinetic parameters significantly depend on the heating rate, as well as on the assumptions adopted in a given calculation method [40]), are at the 36–84 kJ/mol level. The large range of spread suggests that the assumptions associated with this method [37] cause a moderate adaptability of this method to the tested samples. However, at the stage of elaborating on the results of thermal tests in air, a coefficient of determination at the 98–99% level was found for the Coats-Redfern method. The authors of that method used an integration procedure. They obtained the following equation:

$$\ln\left(\frac{\alpha}{T^2}\right) = \ln\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \quad (2)$$

where,

A - Pre-exponential factor (min^{-1})

α - Degree of conversion or fractional mass loss

β - Heating rate (K min^{-1})

E - Apparent activation energy (kJ mol^{-1})

R - Gas constant $8.3136 \text{ (J mol}^{-1}\text{K}^{-1}\text{)}$

T - Temperature (K)

By plotting $\ln\left(\frac{\alpha}{T^2}\right) = f(1/T)$, E value can be calculated. It must be remembered that the equation is only true for zero reaction order, which results from the former simplifications. The results obtained by this method are true for low α , but they can be generalized for the whole process assuming that the reaction mechanism does not change during the reaction duration. From a practical point of view, this method is moderately laborious. It requires taking the α values from the thermogram and doing the necessary calculations for obtaining the plot. Researchers have used this method among others to investigate poly (tetrafluoroethylene) [37] and poly (3-dimethylacryloyloxyethyl) ammonium propanosulfate [41], obtaining results corresponding to the results obtained from other calculating methods.

Comparing the values of activation energy obtained for samples processed by the water- and dew-retting methods, an interesting relationship was found between the average EA measurement results, 65.5 and 40.8 kJ/mol, respectively.

The results of the thermal decomposition analysis of okra fiber samples from different parts of the plant in the presence of oxygen have not yet been published. From the results presented in this publication, it can be concluded that regardless of the origin of the material, okra fibers can be used in composites up to a temperature of 290°C. The activation energy of the decomposition process varies depending on how the fiber is pretreated.

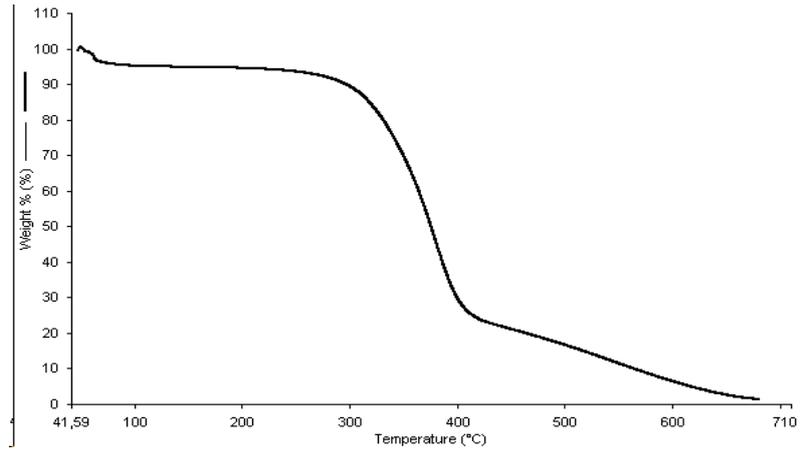
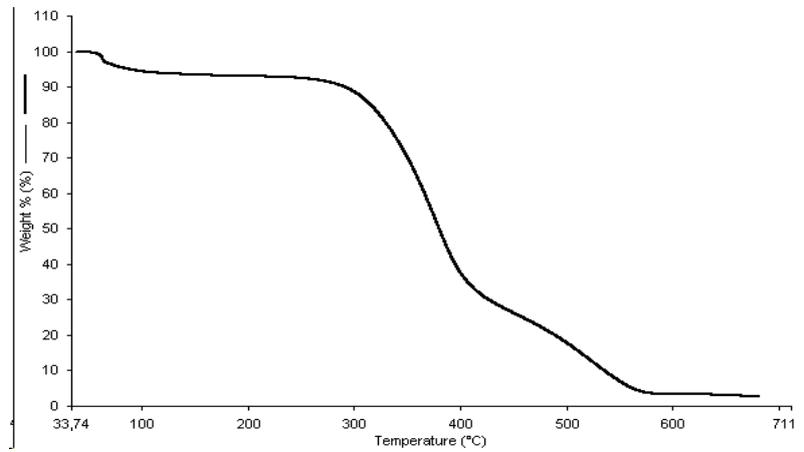
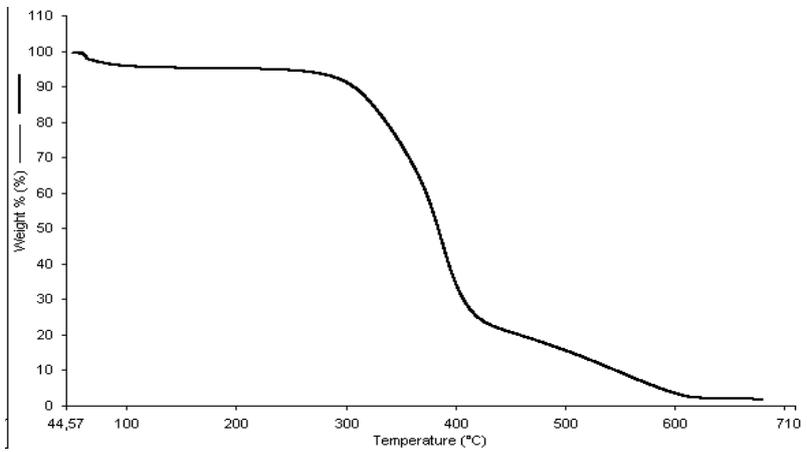
3.4.2. Pyrolysis

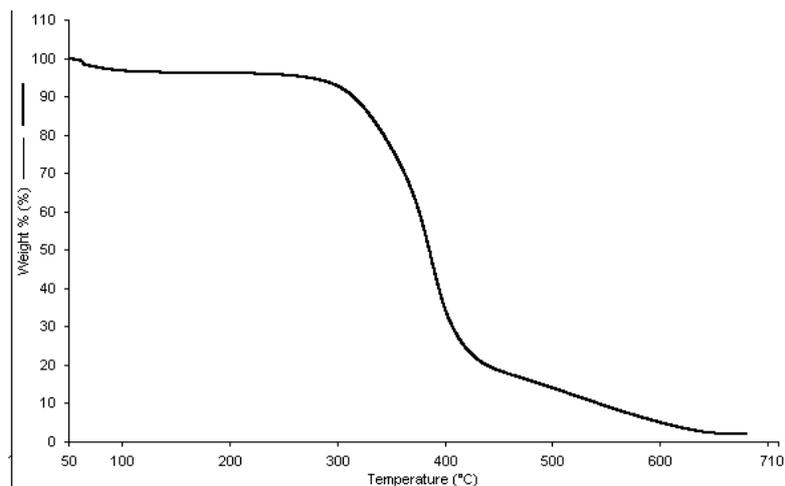
The next stage of thermal research was thermogravimetric analysis in an inert atmosphere. Pyrolysis is a type of thermolysis observed when heating organic materials in an oxygen-free atmosphere. The mechanism of chemical changes occurring during pyrolysis is often very complex, and it can be difficult to study them thoroughly due to the variability of the composition of raw materials subjected to pyrolysis (an example of this can be the description of biomass pyrolysis). As a result of this process, only gaseous products can be formed; however, the process almost always proceeds with the formation of a solid residue.

That the type of atmospheric gas can strongly affect the position of TGA curves on the weight axis has been known for a long time. One of the most attractive features of TGA in an inert atmosphere as a thermal stability analysis method for polymers is that it is almost always possible to glean some information from the data record. The representative thermograms of the samples prepared at ambient conditions for okra are presented in Table 6, and the characteristic degradation temperatures can be found in Table 7.

Table 6. Representative TG curves of analyzed samples.

Sample source	TG curve
Water-retted bottom okra bast fiber	
Water-retted middle okra bast fiber	

Water-retted upper okra bast
fiberDew-retted bottom okra bast
fiberDew-retted middle okra bast
fiber

Dew-retted upper okra bast
fiber**Table 7.** Characteristic temperatures (average values) of main stage thermal degradation of analyzed samples.

Sample	T _{intit}	T _{50%}	T _{final}
BBW	300.0	374.8	406.2
MBW	303.5	389.1	426.3
UBW	299.9	372.4	403.6
BBD	300.0	377.6	406.6
MBD	300.0	382.2	410.9
UBD	299.9	389.7	412.4

According to the data from Tables 6 and 7, the thermal distribution curves of the samples have a two-stage character, similar to the thermo-oxidation processes. Most likely, the first stages are depolymerization and thermal degradation of cellulose macromolecules and the second is afterburning low-molecular breakdown products. The temperatures characteristic of the first, main stage of decomposition are shown in Table 7. The degradation of fibers from different parts of the plant has a very similar character and occurs in similar temperature ranges; differences between individual samples are smaller than for the decomposition process in air. The temperature of half decomposition for bast fibers obtained by the water-retting method is 378.8°C, while for the set with dew-retting it is 383.2°C, which shows the same trend as the thermo-oxidation process.

The main stage of thermal decomposition under neutral conditions was subjected to kinetic analysis. The activation energy values of the decomposition process were calculated using the Coats-Redfern method [37]. The results of the analysis are shown in Table 8.

Table 8. Activation energy of pyrolysis process of okra fibers (standard deviation 4.5%) calculated by Coats-Redfern methods.

Sample	Activation energy [kJ/mol]
BBW	60.4
MBW	50.9
UBW	50.4
BBD	42.8
MBD	54.3
UBD	62.0

The data from Table 8 indicate that EA values under given conditions (in an inert atmosphere) are at the 42.8–73.5 kJ/mol level, i.e. in a much narrower range. The coefficient of determination values are above 99%. Since the decomposition process in an inert atmosphere occurs at a higher temperature than for thermo-oxidation, it is understandable that the average value of activation energy for nitrogen is slightly more than for air (56.6 and 53.0 kJ/mol, respectively).

Literature data showing thermogravimetric curves of okra fiber (without taking into account the part of the plant from which the fiber originated) in an inert atmosphere show a 50% distribution temperature at about 350°C [22] and in the 329.8–349.9°C range (depending on the treatment technique) [23].

Presentation of the main thermal degradation step in the form of $\alpha_s = f(\alpha_r)$ plots (Figure 7) shows very small differences between TG run of each okra sample, which confirms the similar thermal stability of the analyzed samples, as was concluded from the comparison of thermogravimetric curves. However, as one can see in Figure 7, some minor differences can be seen. In ambient conditions, the UBD (dew-retted upper okra bast fiber) sample has slightly higher thermal stability than the reference sample. Taking the $\alpha_s = f(\alpha_r)$ plot into account, fibers can be arranged as follows: UBD > MBD > MBW > UBW > BBW > BBD. As can be seen in Figure 7, this order does not change throughout the whole course of the main thermal degradation stage in nitrogen conditions, which leads to a similar conclusion as for investigation in air, that fibers coming from the middle part of okra bast plant are, very slightly, better in thermal stability than those coming from other parts.

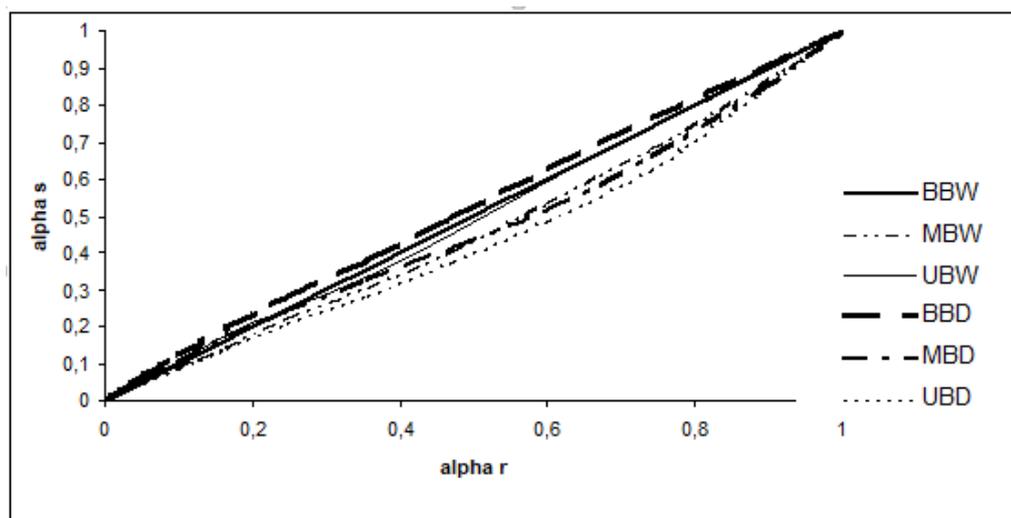


Figure 7. Alpha s – alpha r dependence of okra bast fibers in nitrogen atmosphere.

3.4.3. DSC analysis

Because thermogravimetry techniques allow showing the occurrence of only those processes that are associated with changes in sample mass, to have a full description of the thermal decomposition process and not miss any of the possible processes, a differential scanning calorimetry analysis was also performed. Thanks to the DSC results endo- and exo-energetic changes occurring in tested samples can be observed. Figure 8 contains the DSC thermograms for the tested samples.

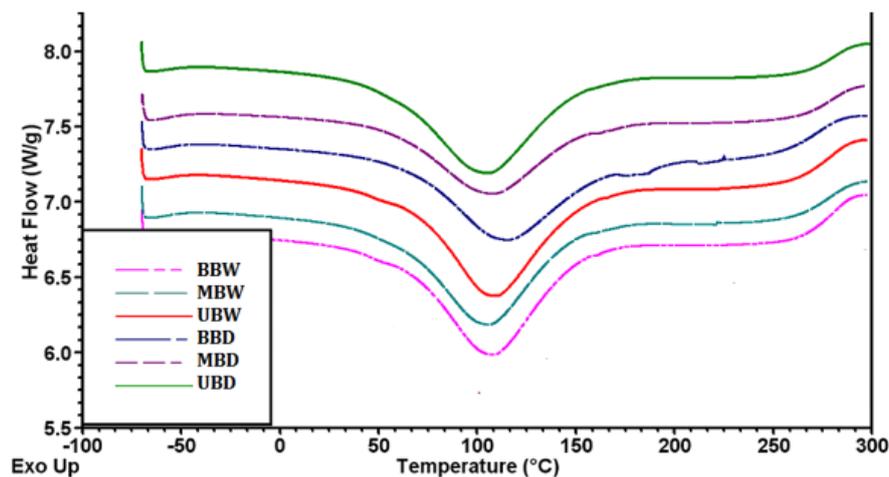


Figure 8. DSC thermograms of okra fibers.

As can be seen from the data in Figure 8, DSC thermograms look very similar; an exothermic signal at 100°C, related to water evaporation, can be seen. Thus, in the -70–300°C temperature range, there are no other changes in the samples of tested materials.

4. Conclusions

The paper describes the results of thermal and physical analyses of okra fiber samples from various parts of the plant's stem. Fibers also differed in how the material was processed to remove non-fibrous components: water-retting and dew-retting. The physical and mechanical properties of the fibers can be summarized as linear density, breaking strength, and elongation at break range between 9.45–17.09 tex, 32.50–51.80 cN/tex, and 2.75–3.48%, respectively. Fibers from the upper part of the okra stem show higher breaking strength and lower linear density, whereas water-retting resulted in higher breaking strength, elongation at break rates, and lower linear density values. The thermal characteristics of all samples were similar, and the differences between the types of fibers were rather small. The main stage of thermal decomposition took place in the 275–400°C temperature range for thermo-oxidation and 300–425°C for pyrolysis. Activation energy values were determined for both processes, obtaining results with a large dispersion of values. The DSC curves of the samples tested show only one exothermic signal, which should be attributed to the evaporation of water. In conclusion, the maximum safe temperature allowing the use of okra fibers as composites is around 275°C in the presence of oxygen.

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