

Enhancement of Oxidative Stabilization of Viscose Rayon Fibers Impregnated with Ammonium Sulfate Prior to Carbonization and Activation Steps

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ABSTRACT: The oxidative thermal stability of microcrystalline plant-based viscose rayon cellulose fiber was improved in the presence of an ammonium sulfate solution. The structural characterization of the oxidized samples was carried out using a combination of fiber thickness, linear density, burning test, X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and infrared (IR) spectroscopy measurements. Oxidized viscose rayon fibers showed physical and chemical transformations with increasing oxidation temperature and were characterized by a reduction in fiber diameter and linear density values together with color changes with increasing oxidation temperature. The results obtained from XRD analysis showed the loss of crystallinity due to the amorphization processes. XRD analysis also showed increasing conversion to a highly crosslinked and cyclized structure with progressing temperature. The DSC and TGA measurements indicated that there was an improvement in thermal stability. The results obtained from IR spectra showed the progress of dehydrogenation and dehydration reactions. IR spectra in the 2000–800 cm^{-1} region showed a loss of crystalline structure confirming the results of XRD. The IR spectra of the oxidized samples also showed the conversion of primary hydroxyl (OH) groups to carbonyl (C=O) groups and the presence of C=C double bonds arising from the formation of a cyclized and crosslinked structure. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

The occurrence of large scale environmental pollution during the last few decades has encouraged scientists to develop advanced materials to selectively decontaminate the environment. Adsorption is one of the preferred methods used due to its efficiency, capacity, and applicability on a large scale.¹ Activated carbon technology, which is one of the most widely used adsorption methods for decontamination, has been found to be one of the most attractive solutions² due to its efficiency.³ Activated carbons are well-known for their extensive surface area, high degree of surface reactivity, and desirable pore size distribution.

Activated carbons are produced using physical and chemical activation methods. Chemical activation has become popular due to its lower activation temperature (usually around 400–500°C) and high carbon yield in comparison with the physical activation process.⁴ It is usually carried out in one step, which consists of the pretreatment of a precursor with chemical reagents followed by carbonization in an inert atmosphere to

simultaneously carbonize and activate the carbon. Physical activation, on the other hand, is usually carried out in two stages. The first stage is the carbonization of a precursor in an inert atmosphere (usually nitrogen) and the second stage is the activation in an oxidizing atmosphere in the presence of carbon dioxide (CO_2), steam, oxygen, or air at temperatures between 800 and 1000°C.

Activated carbon can be produced in granular, powder, and fiber forms. In recent years, activated carbon fiber in the form of woven, knitted, and nonwoven fabrics, due to its porous structure, high micropore volume, high surface area of up to 2500 m^2/g , good mechanical strength, and excellent adsorption and desorption characteristics, has been extensively studied and manufactured commercially since its introduction in the 1960s.⁵ Researchers have studied precursors such as viscose rayon,⁶ polyacrylonitrile,⁷ phenolic resin,⁸ sisal,⁹ hemp,¹⁰ and flax¹¹ fiber as potential replacements for granular and powdery activated carbons due to their better performance in terms of faster adsorption and desorption properties and easier operation.¹²

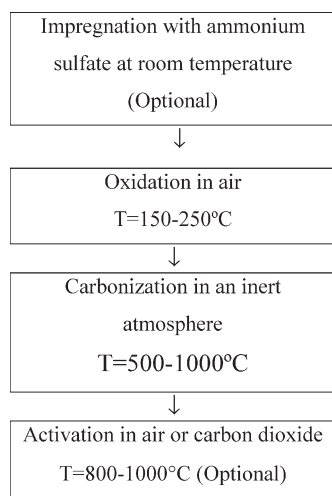


Figure 1. Viscose rayon-based activated carbon fiber production flow chart.

Activated carbon fiber is produced through a series of steps consisting of impregnation with chemicals, oxidation (i.e., thermal oxidative stabilization) in air, carbonization in an inert atmosphere, and the activation of the precursor fibers (Figure 1). The thermal stabilization process is normally carried out in air at temperatures ranging from 200 to 300°C and is a required process to prevent the precursor fibers from melting or degrading during the subsequent carbonization.⁸ Carbonization is carried out at up to 900°C followed by optional physical activation¹³ if no chemical activation is carried out. Physical activation usually follows the carbonization stage.

Oxidation is a necessary step which directly influences the physical and mechanical properties and the microstructure of the final carbon or activated carbon fibers.¹⁴ To improve the carbonization yield and processing rate, low-temperature pyrolysis of viscose rayon is usually carried out in the presence of a reactive atmosphere, such as air or oxygen. Following carbonization and activation, many microsized and nanosized pores form on the surface of the fibers; these play primary roles during the adsorption and desorption processes.^{5,15}

The use of Lewis acids such as zinc chloride and calcium chloride to impregnate cellulose has been studied widely for many years,^{5,16} but they were found to enhance the formation of volatile compounds such as levoglucosan resulting in the reduction of yields during the production of viscose rayon-based activated carbon fibers.⁵ The use of ammonium sulfate with nitrogen was reported to have a flame retardation effect on the burning behavior of viscose rayon fiber.⁵

According to the mechanism proposed by Tang and Bacon,¹⁷ pyrolysis of viscose rayon fibers leads to the formation of a char as a solid residue, high boiling volatiles, and gaseous products.¹⁸ Pyrolysis is characterized by two predominant reactions involving dehydration and depolymerization (i.e., cleavage). Pyrolysis reaction products are formed by two competitive pathways. The first pathway involves the pyrolysis of cellulose leading to chain scissions or depolymerization reactions and the breaking of C—O and C—C bonds within the cellulose rings, accompanied

by the evolution of oxygen-containing compounds¹⁷ which cause major weight losses leading to low carbonization yields. The second pathway is involved with dehydration, rearrangement of the cellulose chains, formation of carbonyl (C=O), carbon-carbon double bonds (C=C), the evolution of CO, CO₂, and the formation of residual char (Figure 2). One way to modify and stabilize the pyrolysis mechanism is to use suitable chemicals such as impregnants or flame retardants which accelerate and catalyze the dehydration reactions with the aim of reducing weight losses, improving the yields, and properties of the final products and achieving higher efficiency.¹⁹

The efficiency and the effect of ammonium sulfate on the oxidative thermal stabilization of viscose rayon-based activated fiber formation have not been reported systematically in previous studies. Therefore, a detailed investigation was necessary to carry out further research on the use of ammonium sulfate as a possible chemical pretreatment with the aim of improving the oxidative stabilization behavior of viscose rayon fiber before the carbonization and activation stages.

The aim of this work was to study the effect of ammonium sulfate pretreatment on the oxidation behavior of viscose rayon fibers at temperatures ranging from 150 to 250°C. Structural characterization was carried out using a combination of fiber thickness, linear density, burning test, X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and infrared (IR) spectroscopy measurements with the aim of monitoring and following the structural transformations as a function of oxidation temperature.

EXPERIMENTAL

Preparation of Oxidized Samples

Untreated viscose rayon multifilament yarn with a linear density of 32.6 tex per 64 filaments was used. Untreated viscose rayon multifilament yarn was treated with 5% (v/v) aqueous ethanol solution for 30 min at 50°C to remove the impurities present on the surface of the fibers followed by a thorough washing under running water for 30 min to remove the final remains. Chemical impregnation was carried out by immersing the samples in 3% (w/v) ammonium sulfate at room temperature for 20 min. The solution had a pH value of 6.8 at 21°C. The ammonium sulfate (99.5% purity) was obtained from TEKKIM Chemicals (Bursa, Turkey). Following the immersion of the samples, each sample was taken out and the excess solution was removed by a towel and dried overnight at 50°C. The pretreated viscose rayon contained 3.4% (w/w) ammonium sulfate on a dry basis. Oxidation was subsequently carried out in an air atmosphere at temperatures of 150, 175, 200, 225, and 250°C for 30 min. The samples were originally wound onto stainless steel frames with the aim of constraining the samples to prevent physical shrinkage and also to prevent the loss of molecular orientation. Oxidative thermal stabilization was carried out with a heating rate of 1°C/min.

Data Collection

The fiber thickness values of the untreated and oxidized viscose rayon fibers were evaluated using a polarizing microscope (Nikon ME600L, Japan) with a calibrated eyepiece. An average

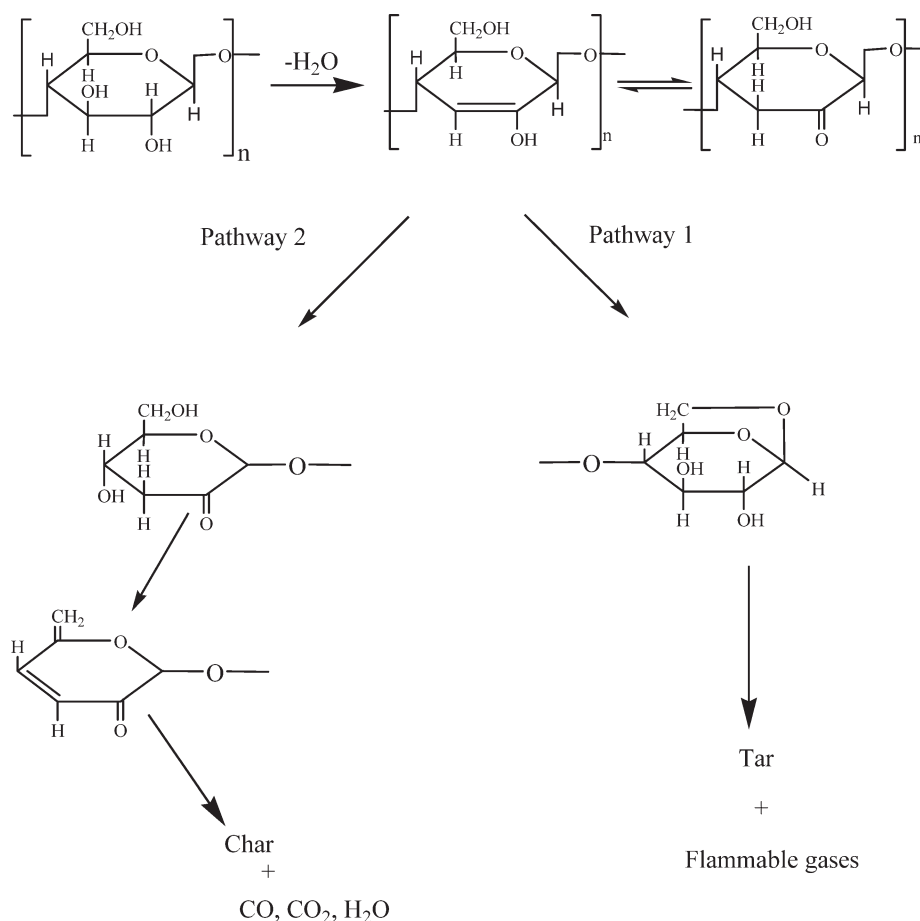


Figure 2. Reactions involved during the pyrolysis of viscose rayon fibers in the presence of a catalyst.¹⁸

of five filaments each with 20 points along the fiber axis direction was used for the thickness measurements.

Linear density is the best way to describe the fineness of fibers. Linear density was determined by measuring the weight in grams per unit length of a multifilament bundle. In the present investigation, tex was used as a linear density; this is defined as the weight of a multifilament bundle in grams per 1000 meters.

Oxidation yield is defined as the ratio of the linear density of the oxidized sample to that of the untreated sample as a function of oxidation temperature. Due to the decomposition of cellulose structure and impregnant during the oxidation step, some volatile substances may be generated which can cause the oxidation yield to be less than 100% for the oxidized samples impregnated with ammonium sulfate. At low temperatures (i.e., room temperature), oxidation yield is expected to be more than 100%,⁵ whereas carbonization yield is defined as the product of oxidation yield and char yield obtained from TGA analysis at 1000°C.

Wide-angle XRD traces were obtained using a Bruker[®] AXS D8 Advance X-ray diffractometer system using nickel filtered CuK_α radiation (λ , 0.154056 nm) and voltage and current settings of 40 kV and 40 mA, respectively. Counting was carried out at 10 steps per degree. The observed equatorial X-ray scattering data were collected in the 5–40° 2 θ range.

The DSC experiments were carried out using a Seiko DSC-6200 EXSTAR system. Typical sample weights used were approximately 5 mg. A heating rate of 10°C/min and an upper temperature range of 450°C were selected. Indium (m.p. 156.6°C and $\Delta H = 28.45$ J/g), was used for heat flow calibration. Indium and zinc (m.p. 419.51°C) standards were used for temperature calibration. The specimens were always tested under a nitrogen flow rate of 50 mL/min.

Thermogravimetric Analysis (TGA) thermograms were collected using a Perkin Elmer Diamond Thermogravimetric/Differential Thermal Analyzer. Typical sample weights used in the measurements were approximately 4–6 mg. A heating rate of 10°C/min and an upper temperature range of 1150°C were selected. The temperature calibration of TG/DTA was carried out using the melting points of indium (m.p. 156.6°C), tin (m.p. 231.88°C), zinc (419.51°C), aluminum (m.p. 660.1°C), and gold (m.p. 1064.18°C) standards. The weight balance calibration was performed by using a standard weight of 20 mg at room temperature in both systems. Experiments were performed under a nitrogen flow of 200 mL/min. Data from TGA were used in the evaluation of weight loss and % char yield for the untreated, ammonium sulfate impregnated, and oxidized viscose rayon fibers.

A Perkin Elmer[®] Spectrum 400 FTIR spectrometer was used for infrared measurements using transmission mode. In all cases, 50

Table I. Characteristics of Oxidized Viscose Rayon Fibers

Oxidation temperature (°C)	Color change	Burning test	Fiber thickness loss (%)	Linear density variation (%)	Oxidation yield (%)
Untreated	White	Fail	0.0	0	100.0
150	Golden yellow	Fail	8.2	-3.4	96.6
175	Brown	Fail	10.7	-4.0	96.0
200	Black	Fail	30.3	-27.0	73.0
225	Black	Pass	33.1	-36.2	63.8
250	Black	Pass	41.3	-44.2	55.8

interferograms of a sample were averaged and transformed with a medium Norton-Beer apodization function. Each sample spectrum was ratioed against a corresponding number of background scans using the same instrument settings. Finally, all the spectra were analyzed using the OMNIC[®] software.

Data Analysis

X-ray Data-Curve Fitting. All the XRD traces obtained from the untreated and oxidized viscose rayon fibers were fitted with a curve fitting procedure developed by Hindeleh et al.²⁰ to separate the overlapping peaks. Each profile is considered to have a combination of Gaussian and Cauchy functions. When the observed and calculated intensity traces converge to the best acceptable parameters, the computer program provides a list of peak parameters in terms of profile function parameter (f), peak height, peak width at half height, and peak position. Curve fitting of the equatorial XRD traces was carried out with three crystalline peaks (110, 110, and 020) and one amorphous peak together with a linear baseline. The peak height of the amorphous contribution was adjusted in such a way that the tail regions fitted very well with the experimental data points. The peak position of the amorphous phase was fixed but half-height width was allowed to vary.

Evaluation of Apparent X-ray Crystallinity. Apparent X-ray crystallinity is based on the ratio of the integrated intensity under the resolved peaks to the integrated intensity of the total scatter under the experimental trace.²¹ This definition can be expressed as follows in eq. (1):

$$\chi_c = \frac{\int_0^\infty I_{cr}(2\theta)d(2\theta)}{\int_0^\infty I_{tot}(2\theta)d(2\theta)} \quad (1)$$

It should be emphasized that the apparent X-ray crystallinity was defined between two arbitrarily chosen angles and should be considered as the optimum mathematical solution. In this work, the apparent X-ray crystallinity was estimated in the 2θ range between 5 and 40°. The region below the baseline is assigned to instrumental background signal which may include air and incoherent scattering.

Evaluation of X-ray Conversion Index. The X-ray conversion index is determined using eq. (2)

$$X - ray - conversionindex(\%) = \frac{\Sigma I_0 - \Sigma I}{\Sigma I_0} \times 100\% \quad (2)$$

where $\Sigma I_0 = I_{110} + I_{110} + I_{020}$ is the sum of the intensities of the 110, 110, and 020 reflections from the untreated viscose rayon

fiber and $\Sigma I = I_{110} + I_{110} + I_{020}$ is the sum of the intensities of the 110, 110, and 020 reflections from the ammonium sulfate impregnated and oxidatively stabilized viscose rayon fiber, respectively. The values of the intensities are obtained after the curve fitting procedure.

RESULTS AND DISCUSSION

Oxidation in an air atmosphere is a recognized step during the manufacture of activated carbon fibers before the carbonization and activation steps of viscose rayon precursors. Oxidation (i.e., oxidative thermal stabilization) enables the precursor fibers to withstand the high temperatures involved during the carbonization stage. In this work, the major focus is placed on the ammonium sulfate impregnation and its effects on the oxidative thermal stabilization process. Ammonium sulfate was used as an impregnant for viscose rayon fiber due to its good flame retardation effects⁵ before the oxidation step.

The oxidation of pretreated viscose rayon fibers containing 3.4% (w/w) ammonium sulfate was performed in an air atmosphere at temperatures ranging from 150 to 250°C for 30 min (Table I). Oxidation in air resulted in the change of the color of the samples from white, through to golden yellow and brown in the early stages to black in the final stages (Table I). The change in the color of the samples can be viewed as an indication of the formation of a stabilized structure. As the oxidation temperature increased to 150°C, the sample acquired a golden yellow color, which is an indication of a chemical reaction taking place. As the temperature increased from 150 to 250°C, the samples acquired darker colors through different shades of brown and finally turned to black after oxidation temperature of 200°C.

Untreated, ammonium sulfate impregnated, and oxidized viscose rayon fibers were exposed to a match flame to assess burning behavior. The results are presented in Table I. The ammonium sulfate pretreated and oxidized samples failed the burning test until the oxidation temperature of 225°C and eventually passed after this temperature. This behavior showed that the samples oxidized at 225°C and above were thermally stabilized and ready for the carbonization and activation steps (Table I).

The fiber thickness of the oxidized samples measured as a function of oxidation temperature is presented in Figure 3(a). The fiber thickness of the oxidized samples with an oxidation temperature of 250°C was reduced from 28.1 to 16.5 μm . The fiber thickness value decreased sharply after an initial oxidation temperature of 175°C and further reduction continued with

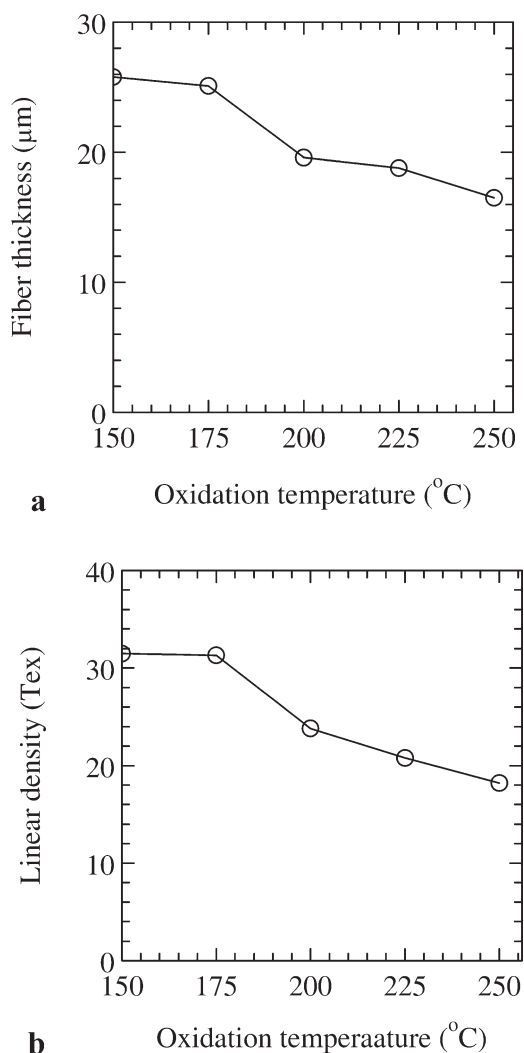


Figure 3. Variation of fiber thickness (a) and linear density (b) of oxidized viscose rayon fibers as a function of oxidation temperature.

progressing oxidation temperature. The most significant reduction in fiber thickness was recorded after an oxidation temperature of 250°C with an approximately 41.3% loss in fiber thickness (Table I) occurring with respect to the untreated sample. The main reason for the severe reduction in fiber thickness was due to the weight loss occurring during the oxidative stabilization stage.

The variation in the linear density of the ammonium sulfate impregnated and oxidized viscose rayon fibers as a function of oxidation temperature is shown in Figure 3(b). Linear density decreased from 32.6 to 18.2 tex with increasing oxidation temperature. A linear density loss of 44.2% was observed after an oxidation temperature of 250°C (Table I). This high level of linear density loss is attributed to the loss of water as part of the dehydration reactions occurring during the oxidation process. Oxidation yield was evaluated and was found to decrease from 97 to 56% with increasing oxidation temperature due to the loss of water occurring during the oxidation stage (Table I).

XRD Analysis

Original viscose rayon fiber is produced as a regenerated cellulose from cotton linters or wood pulp. It consists of cellulose in its polymer structure and its crystal structure is referred to as cellulose II²² as opposed to cellulose I of native cellulose. Viscose rayon fibers are characterized by low crystallinity in comparison with lyocell and modal fibers.²² However, the degree of crystallinity in viscose rayon fibers can be increased by using a low concentration of caustic soda (about 6%)²² and after heat treatment in nitrogen, steam, or water, and particularly after heat treatment in glycerol at temperatures as high as 270°C.^{23,24} Caustic soda treatment of cellulose is also used for the mercerization of native cellulose (cotton) with the aim of improving dimensional stability, luster, and strength.²²

The equatorial XRD traces of untreated, ammonium sulfate impregnated, and oxidized viscose rayon fibers are presented in Figure 4 as a function of oxidation temperature. A qualitative examination of the equatorial XRD trace of untreated viscose rayon fibers shown in Figure 4(a) exhibits three well-defined reflections. A curve fitting procedure was used for the equatorial XRD traces shown in Figure 4 with the aim of obtaining accurate peak parameters. Curve fitting of the equatorial XRD traces was also used to determine the values of apparent X-ray crystallinity, amorphous fraction, and X-ray conversion index as a function of oxidation temperature.

The equatorial XRD trace of untreated viscose rayon fiber shown in Figure 4(a) can be resolved into three crystalline peaks indexed as 110, 110, and 020 reflections, with *d*-spacings of 0.728, 0.441, and 0.405 nm, respectively. These peaks correspond to the monoclinic phase of cellulose II structure with unit cell²⁵ dimensions of *a* = 0.810 nm, *b* = 0.903 nm, *c* = 1.031 nm, and γ = 117.1°. During the curve fitting stage, an additional peak located at approximately 19.4° (*d*-spacing of 0.441 nm) was utilized to improve the fit in the tail regions of the neighboring peaks. This peak has a broad half-height width and behaves as an amorphous peak.

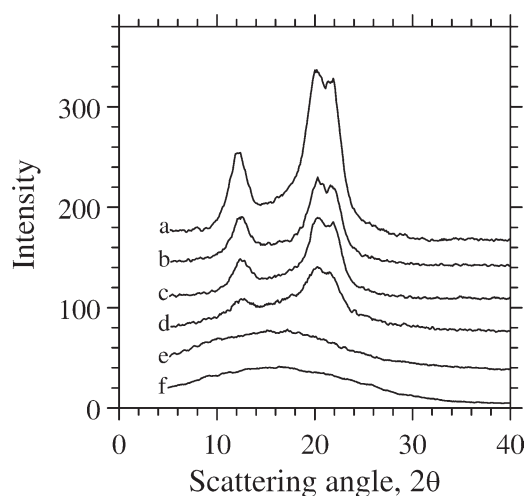


Figure 4. Equatorial XRD traces of (a) untreated and ammonium sulfate pretreated viscose rayon fibers oxidized for 30 min at (b) 150°C; (c) 175°C; (d) 200°C; (e) 225°C; (f) 250°C.

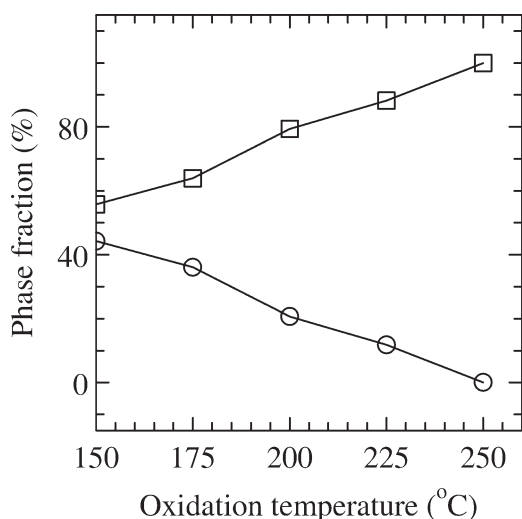


Figure 5. Variation of phase fractions of ammonium sulfate impregnated and oxidized viscose rayon fibers as a function of oxidation temperature. (○) amorphous phase; (□) crystalline (cellulose II) phase.

Ammonium sulfate impregnation followed by oxidation in air at temperatures between 150 and 250°C appeared to have a significant effect on the structure in terms of the degree of crystallinity of the original cellulose II structure. The qualitative examination of equatorial XRD traces presented in Figure 4 showed a gradual disappearance of crystalline structure with increasing oxidation temperature. It is certain that a typical decrystallization (i.e., amorphization) process seems to occur during the oxidation process with increasing oxidation temperature. Intensities of 110, 110, and 020 reflections decreased with increasing oxidation temperature and were totally lost when the oxidation temperature of 225°C was reached. The gradual reduction in the intensity of the 110 reflection with increasing oxidation temperature can be interpreted in terms of the interruption of the interchain hydrogen bonds in the 110 plane and the subsequent relaxation of cellulose rings in the direction of the 020 plane.²⁶

The gradual disappearance of the 020 reflection is thought to be due to the collapsing lattice structure which occurs as part of the decrystallization process taking place during the oxidative stabilization stage. The gradual loss of intensity in the 110 reflection is also thought to be due to the collapsing lattice structure as part of the decrystallization process.

The XRD patterns of the samples oxidized at 225 and 250°C consisted of a broad halolike scatter spreading between scattering angles of 5 and 30°. The half-height widths of the 110, 110, and 020 reflections were broadened with increasing oxidation temperature indicating a decrease in apparent crystallite size. For example the half-height width of the 110 reflection increased from 2.1 to 8.6° when the oxidation temperature was increased from 150 to 250°C. A similar behavior was also observed for the 110 and 020 reflections.

The peak areas obtained from the curve fitting of the equatorial XRD traces shown in Figure 4 were utilized to evaluate the fractions of crystalline (i.e., cellulose II) and amorphous structures

using eq. (1). The results presented in Figure 5 show a decreasing apparent X-ray crystallinity and an increasing amorphous fraction as a function of oxidation temperature. Apparent crystallinity (i.e., fraction of cellulose II phase) decreased from 41 to 0% after oxidation at 250°C, whereas the amorphous phase increased from 59 to 100% after oxidation at 250°C.

A new method of evaluating the X-ray conversion index using the peak heights of the 110, 110, and 020 reflections was evaluated using eq. (2). The results presented in Figure 6 show the values of the X-ray conversion indices for the oxidized viscose rayon fibers as a function of oxidation temperature. The X-ray conversion index increased from 48 to 100% when the oxidation temperature increased from 150 to 250°C. The X-ray conversion index values were found to increase with increasing oxidation temperature and can be viewed as a reliable technique to evaluate the amount of crosslinked structure forming during the oxidation stage.²⁷ The results clearly indicate that ammonium sulfate impregnation followed by oxidation in air led to the disappearance of the crystalline structure and an increase in the amorphous phase fraction together with an increase in the fraction of crosslinked ladderlike structure containing aromatic moieties.

Analysis of DSC Measurements

The DSC technique was used to assess and monitor the thermal behavior of oxidative thermal stabilization in untreated and oxidized viscose rayon fibers impregnated with ammonium sulfate at oxidation temperatures ranging from 150 to 250°C. The DSC thermogram of untreated viscose rayon presented in Figure 7(a) shows a broad endotherm near 100°C due to the evaporation of moisture caused by the presence of physically absorbed water. The behavior of this endotherm is caused by the hydrophilic nature of the cellulose structure. This endotherm is followed by a stronger but somewhat broader endotherm extending from 280 to 340°C with a peak temperature of 328°C attributed to the decomposition (depolymerization) of cellulose.²⁸

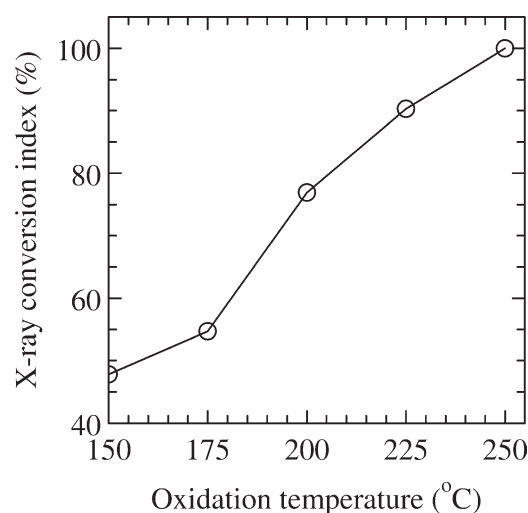


Figure 6. Variation of X-ray conversion indices of untreated and ammonium sulfate pretreated and oxidized viscose rayon fibers as a function of oxidation temperature.

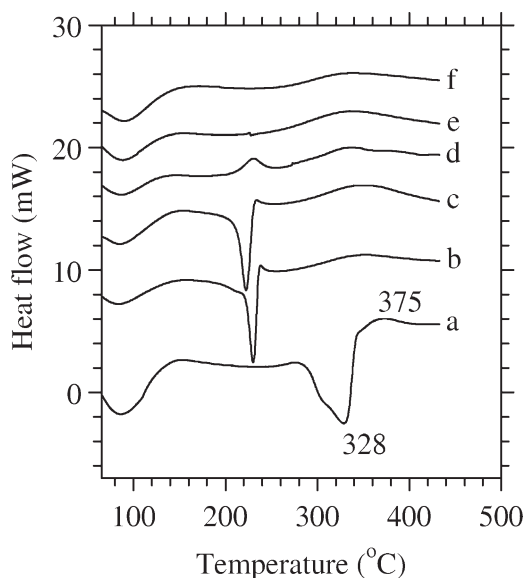


Figure 7. DSC thermograms of untreated (a) and ammonium sulfate impregnated and oxidized viscose rayon fibers for 30 min as a function of oxidation temperature. (b) 150°C; (c) 175°C; (d) 200°C; (e) 225°C; (f) 250°C.

The DSC thermogram in Figure 7(a) exhibits an additional peak as a broad exotherm extending from 350 to 400°C with a maximum peak temperature of 375°C due to the oxidation of levoglucosan decomposition by products.²⁹

As already shown by the thermal behavior of untreated viscose rayon, pyrolysis of cellulose is strongly associated with dehydration and depolymerization reactions. The depolymerization of untreated cellulose results in the formation of levoglucosan which can evaporate showing an endothermic reaction or undergo aromatization showing an exothermic reaction.³⁰

Ammonium sulfate impregnation followed by oxidative stabilization in air appeared to have a strong effect on the DSC thermograms of oxidized viscose rayon fibers. Figures 7(b–f) show the DSC thermograms of ammonium sulfate impregnated viscose rayon fibers oxidized in air between 150 and 250°C for 30 min. All DSC thermograms showed an endotherm around 100°C due to the evaporation of absorbed water. The DSC thermogram of the sample oxidized at 150°C showed a cellulose depolymerization endotherm located around 230°C which appeared to have shifted from 328°C due to the ammonium sulfate impregnation. This is a net cellulose decomposition temperature reduction of 98°C. The breadth of this endotherm also narrowed. This behavior clearly shows the net effect of ammonium sulfate impregnation on decomposition temperature. The DSC thermogram of the sample oxidized at 175°C showed that the cellulose decomposition temperature fell to 220°C with a net reduction of 108°C. The large reduction in cellulose decomposition temperature on ammonium sulfate impregnation may be attributed to a reduction in the degree of crystallinity (i.e., increase in amorphous fraction)³¹ with increasing oxidation temperature.

The area under the cellulose decomposition endotherm decreased with increasing oxidation temperature and disappeared completely at the oxidation temperature of 200°C and

above. The reduction and eventual disappearance of the decomposition endotherm is clear evidence of the effect of ammonium sulfate impregnation on the retardation of depolymerization reactions occurring during oxidative thermal treatments. As will be shown later, this behavior may explain the reasons behind the increased char yields following ammonium sulfate impregnation.

When the oxidation temperature increased to 200°C, DSC thermogram showed the disappearance of cellulose decomposition reactions. This means that the pyrolysis reactions no longer show the formation and evaporation of levoglucosan. The presence of an exothermic peak at 230°C is a clear indication of the occurrence of aromatization reactions due to the presence of residual levoglucosan at the oxidation temperature of 200°C. The disappearance of the cellulose decomposition endotherm at an oxidation temperature of 200°C also indicates the formation of a thermally stabilized structure. The DSC thermograms of the samples oxidized at 225 and 250°C showed that the decomposition endotherms totally disappeared due to the cellulose II structure.

The results showed the suppression and ultimately the prevention of the formation of levoglucosan at an oxidation temperature of 225°C and above together with the added advantage of increasing thermal stability before the carbonization and activation steps. The results suggest the formation of crosslinked and cyclized structures at oxidation temperatures of 225 and 250°C with the total elimination of the cellulose II structure.¹⁷

The pyrolysis of untreated viscose rayon proceeds predominantly by depolymerization as suggested by low char yield.¹⁷ In the presence of ammonium sulfate acting as a catalyst, the dehydration reaction is expected to be favored over depolymerization. Impregnation with ammonium sulfate is expected to increase the char yield due to the occurrence of predominantly favorable dehydration reactions.¹⁷ Dehydration reactions are the processes involving the splitting off of a hydroxyl group and of a hydrogen between two hydroxyl groups to form water.³²

Thermogravimetric Analysis

In this work, TGA was extensively utilized for the thermal characterization of the oxidative thermal stability of untreated and ammonium sulfate impregnated viscose rayon fibers oxidized in an air atmosphere. Fast carbonization under an inert atmosphere is undesirable for the formation of viscose rayon-based carbon fibers or activated carbon fibers. This is expected to result in the formation of undesirable side-reactions releasing volatile carbon-containing substances leading to low carbon yield.⁵

The effect of ammonium sulfate impregnation on the pyrolysis behavior of viscose rayon fibers oxidized in air at different temperatures can be quantitatively characterized by TGA. Weight loss and char yields can be utilized to compare the relative yields of the carbonization step as a function of oxidation temperature.

According to Li et al.,¹⁸ ammonium sulfate decomposition occurs between 260 and 420°C. It has been shown³³ that ammonium sulfate decomposes in two steps. In the first step at

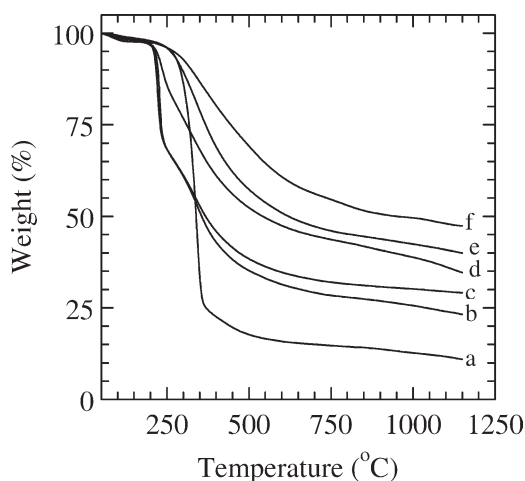
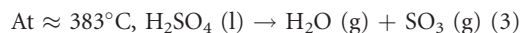
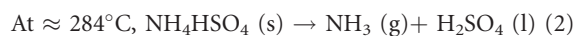
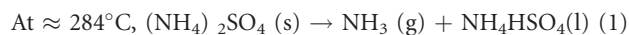


Figure 8. TGA thermograms of untreated (a) and ammonium sulfate pretreated viscose rayon fibers oxidized for 30 min as a function of oxidation temperature (b) 150°C; (c) 175°C; (d) 200°C; (e) 225°C; (f) 250°C.

around 284°C, ammonia (NH_3) formation takes place through reactions (1) and (2). The second reaction proceeds through reaction (3) at 383°C with the formation of water and SO_3 groups. It seems that during the pyrolysis reactions, formation of sulfuric acid catalyzes the dehydration of cellulose rings through the primary hydroxyl group ($-\text{CH}_2-\text{OH}$) by forming cellulose sulfate ester groups.



The formation and subsequent elimination of sulfate ester is expected to prevent the formation of levoglucosan leading to increased yield and efficiency.

The TGA thermograms of untreated, ammonium sulfate impregnated, and oxidized viscose rayon fibers are presented in Figure 8 as a function of oxidation temperature. All TGA thermograms showed weight losses around 100°C representing the evaporation of moisture caused by physically bound water. After this point, untreated viscose rayon [Figure 8(a)] showed no significant weight loss up to 300°C; then, after this point, the rate of weight loss increased rapidly between 300 and 375°C followed by slow weight losses up to 1150°C.

Ammonium sulfate impregnated and oxidized viscose rayon fibers [Figures 8(b–f)], on the other hand, showed remarkably different thermal behavior. The TGA thermograms of the oxidized samples showed reduced weight loss with increasing oxidation temperature indicating increasing char yield due to the increasing crosslinking density between cellulose chains. The untreated sample lost weight over a narrow temperature range, whereas the oxidized samples lost weight over a wider temperature range due to the increased crosslinking-related ladderlike structure formation. Weight losses due to cellulose depolymerization for the samples oxidized at 150, 175, and 200°C appear to occur at lower temperatures than for the untreated sample (Figure 8), whereas the samples oxidized at 225 and 250°C

showed higher cellulose decomposition temperatures than untreated sample. The TGA thermograms of samples oxidized at 150 and 175°C showed two step decomposition reactions: a low temperature process at 200–240°C, which is in agreement with DSC data, and a high temperature process at 300–600°C; whereas those samples oxidized between 200 and 250°C showed single-step decomposition behavior (Figure 8).

The TGA thermograms indicated slower weight loss for the oxidized samples in the temperature region of 250–550°C due to crosslinking and aromatization reactions. The residues at 1000°C were found to be higher for the ammonium sulfate impregnated and oxidized viscose rayon fiber, indicating higher yields during the pyrolysis (i.e., carbonization) stage.

Figure 9 shows the comparison of the char yields at 500 and 1000°C obtained from the untreated and oxidized viscose rayon fibers. The results show an increasing char yield with increasing oxidation temperature. Char yields at 500°C are found to be higher than those at 1000°C ranging from 35.2 to 69.2% for the oxidation temperatures from 150 to 250°C. Char yield reached a maximum value of 49.5% at 1000°C for the ammonium sulfate pretreated viscose rayon fibers oxidized at 250°C.

According to Tang and Bacon,¹⁷ the final residue consists of four-carbon building blocks originating directly from the original cellulose structure. As a result, the maximum carbonization yield should be around 29.5%. This means that the upper weight loss should be around 70.5%. The carbonization yield evaluated from oxidation yield and char yield gave values between 24.7 and 28.5% (Figure 9) which is in agreement with the results of Tang and Bacon.¹⁷

TGA analysis demonstrated that the ammonium sulfate impregnated and oxidized viscose rayon fibers acquire higher thermal stability than the untreated fiber as a result of the oxidation-based crosslinking reactions.

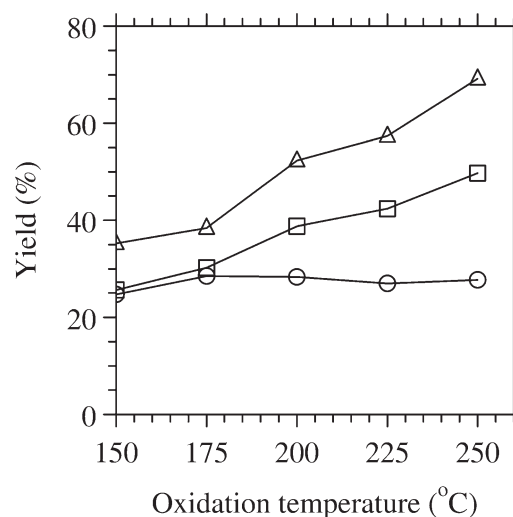


Figure 9. Variation of char yields at 500°C (Δ) and 1000°C (\square) and carbonization yield at 1000°C (\circ) of oxidized viscose rayon fibers as a function of oxidation temperature.

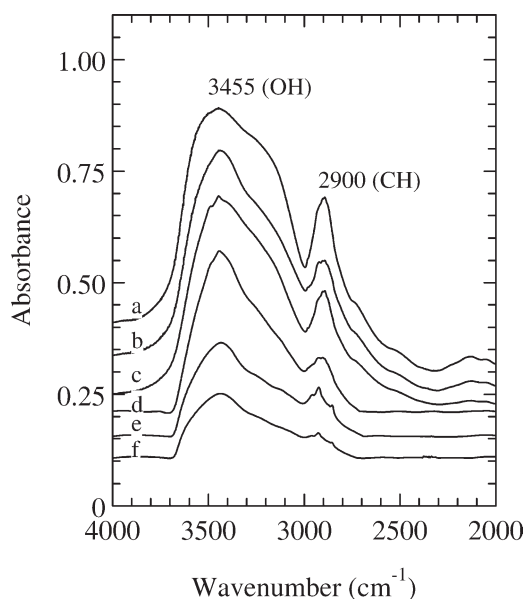


Figure 10. IR spectra of untreated (a) and ammonium sulfate impregnated viscose rayon fibers oxidized in air for 30 min as a function of oxidation temperatures in the 4000–2000 cm^{-1} region. (b) 150°C; (c) 175°C; (d) 200°C; (e) 225°C; (f) 250°C.

The obtained results indicate strong interactions between ammonium sulfate and the hydroxyl groups of viscose rayon fibers during the oxidation step and these resulted in the formation of intramolecular and possibly intermolecular crosslinks leading to the formation of a large amount of carbonized structure in an inert atmosphere.

Analysis of IR Spectroscopy Measurements

In this work, IR spectroscopy was extensively used to follow and monitor the nature of the chemical transformations taking place during the oxidative thermal stabilization treatment. The intensity and spectroscopic changes were examined as a function of oxidation temperature. The IR spectra of the untreated and oxidized samples corresponding to the 4000–2000 cm^{-1} region are shown in Figure 10 as a function of oxidation temperature.

The region between 4000 and 3000 cm^{-1} is assigned to free and intramolecular hydrogen bonded OH groups in cellulose II. CH stretch vibrations are located in the 3000–2800 cm^{-1} region. The hydroxyl groups of the cellulose structure are the reaction sites with ammonium sulfate. Following ammonium sulfate impregnation and oxidative stabilization in an air atmosphere, the IR spectra showed distinct intensity changes, especially the bands associated with the OH and CH stretching in the 3800–2800 cm^{-1} region and cellulose II bands located in the 2000–800 cm^{-1} region.

As the oxidation temperature increased, OH and CH vibrations at 3455 and 2900 cm^{-1} gradually lost their intensities but never completely disappeared. The CH band also lost its intensity with progressing oxidation temperature, but a minor amount still remained, indicating that not all hydrogen atoms take part in dehydrogenation reactions. The loss of OH groups and

hydrogen from CH groups is clear evidence that dehydration reactions occurred during the oxidation process.

The IR spectra of the untreated and oxidized samples are shown in Figure 11 as a function of oxidation temperature in the 2000–800 cm^{-1} region. The IR spectra of the oxidized samples show the presence and formation of a new peak located at 1715 cm^{-1} assigned to carbonyl (C=O) stretching as a shoulder at the oxidation temperature of 175°C; this gradually and progressively strengthened between oxidation temperatures of 175 and 250°C (Figure 11). It seems that primary hydroxyl groups of cellulose rings are converted to carbonyl (C=O) groups as a result of the role played by the catalyzing action of ammonium sulfate during the oxidation process.³⁴ The formation of oxygen containing functional groups plays an important role in the thermal stabilization process.

The IR band at 1650 cm^{-1} assigned to OH stretching of physically absorbed water also loses its intensity with increasing oxidation temperature. This indicates the physical dehydration of samples with increasing oxidation temperature.

The IR spectra of oxidized samples also show the formation of a new band at 1600 cm^{-1} assigned to C=C double bonds as a shoulder at the oxidation temperature of 200°C which progressively and gradually increased its intensity (Figure 11). The intensity of the C=C stretching band becomes predominant in the IR spectra of the samples oxidized at 225–250°C indicating that the oxidized cellulose contains highly crosslinked and aromatized structures in agreement with the DSC results mentioned before.

The cellulose II crystalline bands at 1424 cm^{-1} assigned to CH₂ symmetrical bending and 1380 cm^{-1} assigned to CH bending

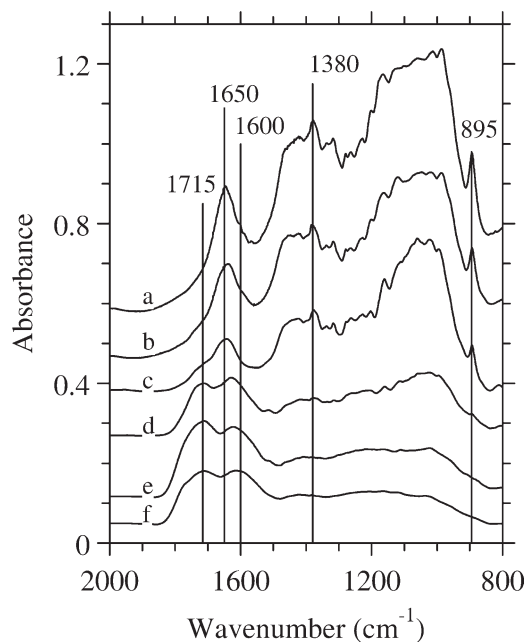


Figure 11. IR spectra of untreated (a) and ammonium sulfate impregnated viscose rayon fibers oxidized in air for 30 min as a function of oxidation temperatures in the 2000–800 cm^{-1} region. (b) 150°C; (c) 175°C; (d) 200°C; (e) 225°C; (f) 250°C.

lost their intensities gradually with progressing oxidation temperature. This behavior of the crystalline bands clearly indicates the loss of order as part of the amorphization (decrystallization) process with increasing oxidation temperature. This is also in agreement with the XRD results mentioned before.

All the IR bands in the 1350–950 cm^{-1} range lost their intensity indicating the loss of crystalline cellulose structure with increasing oxidation temperature. The IR band at 895 cm^{-1} assigned to C—O—C stretching of the cellulose ring also lost its intensity with increasing oxidation temperature and disappeared completely at the oxidation temperature of 200°C and above, indicating the complete destruction of the cellulose ring as part of cyclization and aromatization reactions.

The results obtained so far confirm that ammonium sulfate catalyzed the dehydrogenation and dehydration reactions while suppressing the depolymerization reactions. It is clear that ammonium sulfate impregnation caused crosslinking reactions and aromatization at lower temperatures than in its absence. It also depressed the formation of tar and volatile substances while resulting in a high carbonization yield, which is in agreement with the results obtained from thermal analysis (DSC and TGA) as mentioned before.

The hydroxyl (OH) groups of viscose rayon acted as the reaction sites with ammonium sulfate. During the oxidative stabilization, the primary hydroxyl (OH) groups of the cellulose chains were converted to carbonyl (C=O) groups, which prevented the formation of levoglucosan and led to enhanced carbonization yield as mentioned before during the TGA analysis.

CONCLUSIONS

Improvement in the oxidative thermal stability of viscose rayon fibers was obtained when the samples were impregnated with an ammonium sulfate solution followed by oxidation in air at temperatures between 150 and 250°C. Physical and chemical changes were investigated in greater detail. The structural analysis of oxidized viscose rayon fibers was carried out using a combination of fiber thickness, linear density, burning test, XRD, DSC, TGA, and IR spectroscopy measurements. The oxidized viscose rayon fibers showed physical and chemical changes with temperature and were characterized by a reduction in fiber diameter and linear density values together with color changes with increasing oxidation temperature. The viscose rayon fibers were properly stabilized at an oxidation temperature of 225°C and above. The results obtained from XRD analysis showed the loss of crystalline structure and also showed conversion of the original cellulose chains to a highly crosslinked and cyclized structure with temperature. The DSC thermograms showed a clear reduction in decomposition temperature in the early stages of oxidation followed by the retardation of decomposition reactions in the later stages. The results also showed the cyclization and crosslinking reactions occurring after the oxidation temperature of 225°C. The DSC and TGA measurements indicated that there was an improvement in thermal stability. The TGA results showed a char yield of up to 49.5% and a carbonization yield of up to 28.5% at

1000°C. The results obtained from IR spectra showed that the gradual and progressive loss of intensity of OH and CH vibrations was closely associated with dehydrogenation and dehydration reactions. The IR spectra showed the loss of crystalline structure confirming the results of XRD, as well as the conversion of primary hydroxyl (OH) groups to carbonyl (C=O) groups responsible for thermal stabilization and the presence of C=C double bonds arising from the formation of a cyclized and crosslinked structure.

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