

## Oxidation and pyrolysis of chitosan as a route for carbon fiber derivation

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Received 9 August 2001; revised 10 January 2002; accepted 10 January 2002

### Abstract

The oxidation and pyrolysis of chitosan were studied with the aim of obtaining carbon fibers from chitosan fibers. The effect of heat treatment temperature and time as well as pretreatment with ammonium chloride on the conversion process was analyzed. The mechanism for the conversion of chitosan to carbon during oxidation, suggested by FTIR analysis, is one where degradation takes place together with decomposition of the pyranose ring with partial dehydration and deamination. Pretreatment of chitosan improved the carbon yield significantly in the end product. Improved tensile strengths were observed upon pyrolysis. Although the heat treatment temperatures were considerably low, a higher C yield was obtained with chitosan fibers compared to rayon fibers (>20 vs. 15%, respectively). It is concluded that pyrolysis of chitosan fibers in an inert atmosphere can be an alternative method for the production of carbon fibers with regard to pyrolysis of cellulose (rayon) fibers. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Chitosan; Oxidation; Pyrolysis; Carbon fiber

### 1. Introduction

There is growing interest at international level in natural resources and environmental-friendly processes. Increasing levels of pollution and destruction of natural resources creates concern among industrial, public, and scientific communities. Driven by the need for alternative resources, processes, and products that are harmless or less harmful to the environment, extensive research is being conducted. Natural and renewable polymers such as cellulose, agarose, and chitin find new applications due to their availability and environmental compatibility. Chitosan, a derivative of chitin, has already found many diverse applications such as medicine, cosmetics, food technology, and biotechnology (Peter, 1995).

Chitin is a natural polymer second largest after cellulose in abundance (Peter, 1995). It is derived from crustacean shells, a by-product of lobsters, crabs, and the likes. Other natural sources of chitin such as yeasts, fungi, and insects also exist. Chitosan is obtained from chitin by deacetylation using strong alkali solutions (Muzzarelli, 1977). It is more extensively studied and technologically more important

than chitin due its higher versatility, for example in terms of solubility in various solvents such as dilute aqueous acids.

The production of carbon fibers from cellulose (or rayon, which is cellulose in fiber form) is well established (Bracke, Schurmans, & Verhoest, 1984; Chawla, 1987). Cellulose is the third largest source of carbon fibers after polyacrylonitrile (PAN) and pitch. The process for carbon fiber production starts with an oxidation or stabilization step at a temperature between 300 and 400 °C in an oxidizing atmosphere (air or oxygen), where the structure is converted to a form which is stable at higher temperatures (Chawla, 1987; Savage, 1993). At this stage, chain fragmentation occurs. The precursor rayon fibers may be treated with dilute phosphoric acid or ammonium chloride, which serve to reduce the oxidation step from several hours to 5 min. After oxidation, the fibers are heat treated under an inert atmosphere for pyrolysis at a temperature of 1000–1500 °C. This step is called carbonization. Further heat treatment at higher temperatures (up to 2800 °C) may be applied for graphitization. Additionally, stretching of fibers during graphitization is possible for improved elastic modulus, but is an expensive process. Due to their low strength and low C yield, rayon-based fibers have been abandoned for high-strength applications in favor of PAN and pitch based C-fibers. However, they are widely used in ablative

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Table 1  
L8 matrix for oxidation experiments

Experiment no.	Temperature (°C)	Time (min)	Pretreatment <sup>a</sup>
1	300	60	–
2	300	60	+
3	300	360	–
4	300	360	+
5	400	60	–
6	400	60	+
7	400	360	–
8	400	360	+

<sup>a</sup> – No pretreatment, + pretreated with NH<sub>4</sub>Cl.

technology, as activated carbon fibers, and other C-textile products.

Since chitosan is a polysaccharide, like cellulose, the possibility of producing carbon fibers from chitosan seemed quite high. Chitosan may have some advantages over cellulose in the production of carbon fibers, such as higher yield and better mechanical properties, due to its structural differences from cellulose (Kumar, 2000). The ability to synthesize a large variety of chitosan derivatives is also an advantage for further studies aiming at obtaining new materials or processes using pyrolysis of these derivatives. Thus, the present study aimed at investigating the potential of chitosan fibers as a precursor for carbon fibers and obtaining a thorough understanding of the effect of various process parameters on the carbon yield.

## 2. Experimental

### 2.1. Oxidation and pyrolysis

Chitosan fiber was obtained from R C Biochemical Co. Korea,<sup>1</sup> with the following properties: degree of deacetylation 90–95%, tenacity 2.1 g/d, fiber diameter 20–50 µm, elongation 15–25%. Chitosan powder, used for comparative experiments, was obtained from Primex Co. Norway, with 60 mesh particle size, food grade purity, and a degree of deacetylation of 90%. The viscosity average molecular weight of the fiber and the powder were  $1.8 \times 10^5$  and  $3.0 \times 10^5$ , respectively. The Taguchi design of experiments approach (Roy, 1990) was used for the selection of experimental conditions since the range of unknown process parameters was too large initially. This approach provides a means to efficiently pinpoint of those process parameters, which have a significant impact on the expected output. From well-developed conditions used for the conversion of cellulose (rayon) and polyacrylonitrile (PAN) fibers to carbon fibers (Bracke et al., 1984; Chawla, 1987; Savage, 1993), it was established that the potentially important process parameters for maximum carbon yield are tempera-

ture and time for oxidation and carbonization as well as the application of pretreatment. L8 design matrices were used for oxidation and pyrolysis experiments as given in Tables 1 and 2, respectively. The upper and lower levels of process parameters were estimated from process conditions used in similar processes (Bracke et al., 1984; Chawla, 1987; Savage, 1993) and some preliminary experiments. A set of pyrolysis experiments was conducted with oxidized samples with and without pretreatment while another set of identical experiments was conducted using direct pyrolysis of chitosan with no oxidation step in between, following the same schedule given in Table 2. A full range of oxidation and subsequent pyrolysis treatments were equally applied to chitosan in the powder form. Additional runs of oxidation treatment at 300 and 400 °C were made with chitosan powders and fibers with 5 min intervals up to 30 min, 10 min intervals up to 60 min, and hourly intervals up to 6 h, in order to observe the mass reduction.

Pretreatment of chitosan involved application of sufficient amounts of  $1 \times 10^{-3}$  M ammonium chloride (Merck) that would coat the fibers or powders for 15 min before the start of heat treatment. Oxidation was performed in a box type furnace within Pt crucibles in air. Pyrolysis was applied in flowing nitrogen in a copper tube without an interlayer in the case of fibers, and in graphite boats in the case of powders. Grafoil<sup>®</sup> graphite foil (Graftech-Union Carbide, Cleveland, OH) was used for preparation of these boats. This product provided easy shaping and a non-stick environment for chitosan for easy separation after heat treatment. All eight experiments of pyrolysis of oxidized samples were applied to samples oxidized at 400 °C for 1 h, with and without pretreatment. The selection of these precursors was based on FTIR results. The lower and upper ranges of pyrolysis temperatures were 500 and 700 °C, respectively. These temperatures are the lower regions of possible pyrolysis temperatures in comparison with rayon → carbon conversion and they were selected to establish the possibility of applying lower (hence less costly) process temperatures. Samples were weighed, before and after each heat treatment, with a precision balance.

Table 2  
L8 matrix for pyrolysis experiments

Experiment no.	Temperature (°C)	Time (min)	Pretreatment <sup>a</sup>
1	500	6	–
2	500	6	+
3	500	60	–
4	500	60	+
5	700	6	–
6	700	6	+
7	700	60	–
8	700	60	+

<sup>a</sup> – No pretreatment, + pretreated with NH<sub>4</sub>Cl before oxidation only.

<sup>1</sup> R C Biochemical Co., Ltd., Manufacturer's data.

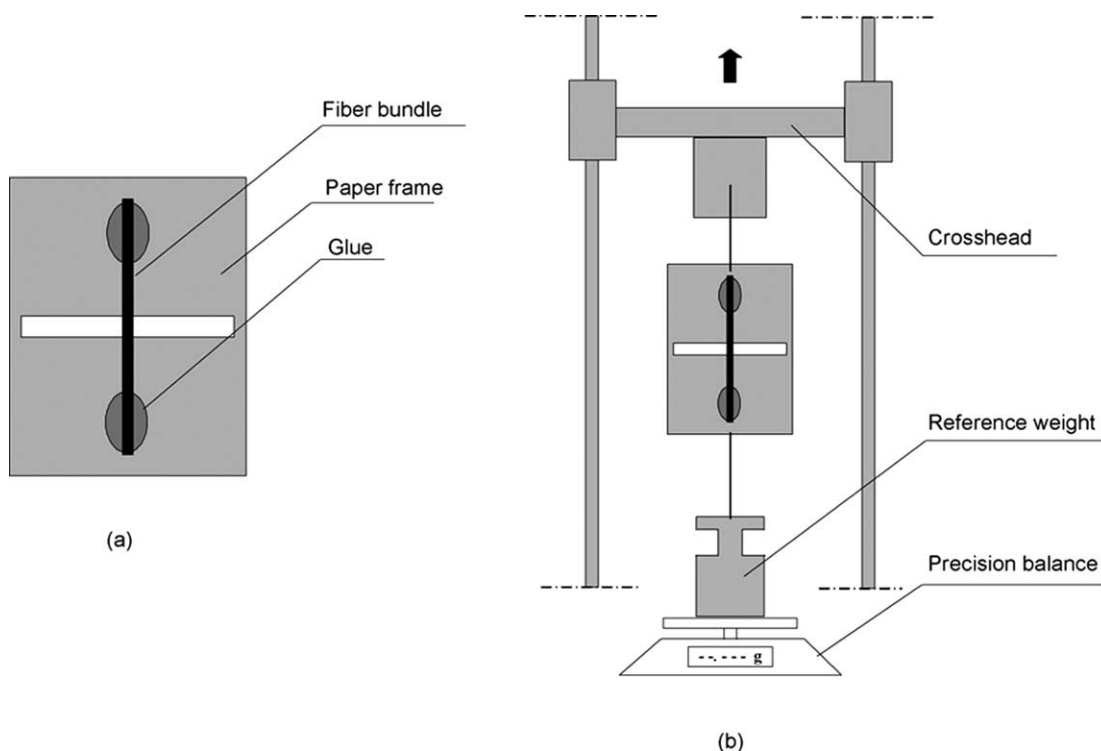


Fig. 1. Experimental set-up for tensile testing of fiber bundles.

## 2.2. Instrumental analysis

FTIR analysis was conducted by a Mattson Satellite 5000 FTIR Spectrophotometer. The samples were analyzed in KBr pellets. Elemental analysis was conducted by a CHNS-932 (LECO) analyzer at TUBITAK—Scientific and Technical Research Council of Türkiye.

X-ray diffraction (XRD) of as received powders and fibers was used to compare the crystallinity of both types of chitosan. A Scintag-LET 2400 model powder diffractometer with Cu K $\alpha$  radiation was used. The fibers were randomly oriented during sample preparation for XRD in order to prevent orientation effects.

Differential thermal analysis (DTA) of as received and pretreated powder and fiber samples was conducted under flowing N<sub>2</sub> atmosphere up to 1400 °C using a DuPont Model 910 DTA/DSC analyzer. All the samples were subjected to a heat treatment at 200 °C for 30 min in order to cancel any humidity related noise. Thermal gravimetric analysis (TGA) up to 800 °C was additionally applied to selected samples using a General V4 1C DuPont 2000 instrument.

Molecular weights of the samples were measured by dilute solution viscometry using an Ubbelohde type viscometer. The intrinsic viscosities of chitosan samples were determined at 30 °C in 0.2 M CH<sub>3</sub>COOH/0.1 M CH<sub>3</sub>COONa buffer solution. The molecular weights were calculated using the Mark-Houwink equation and taking  $K$  and  $\alpha$  values as  $6.589 \times 10^{-3}$  g/ml and 0.88 (Wang, Bo, Li, & Qin, 1991).

Tensile testing was applied to fiber bundles composed of

up to 100 individual fibers in each test. Each fiber bundle was glued to a piece of stiff paper frame with some strong glue (Fig. 1a) (Venkatesh, 1993). The length between the glued points was 6 mm and only those samples, which failed within that region, were taken into consideration for tensile strength calculations. This assembly was then connected to the cross-head of the tensile testing machine (J.J. Instruments) on one end and to a reference weight on the other (Fig. 1b). During the slow (6 mm/min) ascent of the cross-head, the decrease in the weight, placed on top of a precision balance, was tracked. The minimum weight read from the balance corresponds to the maximum weight decrease in the reference weight, and thus, to the fracture load of the fiber bundle. The tensile strength was calculated from this load and the total cross-sectional area of fibers in each bundle. After careful alignment of the paper frames, the two sides of the paper frame were carefully cut to transfer the load to the fibers. Misalignment normally leads to premature failure since the fibers were very fragile after heat treatment. Therefore, sample preparation requires special care and is time consuming.

## 3. Results and discussion

### 3.1. FTIR analysis

Several workers studied thermal degradation of chitosan up to temperatures of 240 °C. These studies revealed that heat treatment up to 160 °C did not significantly change the

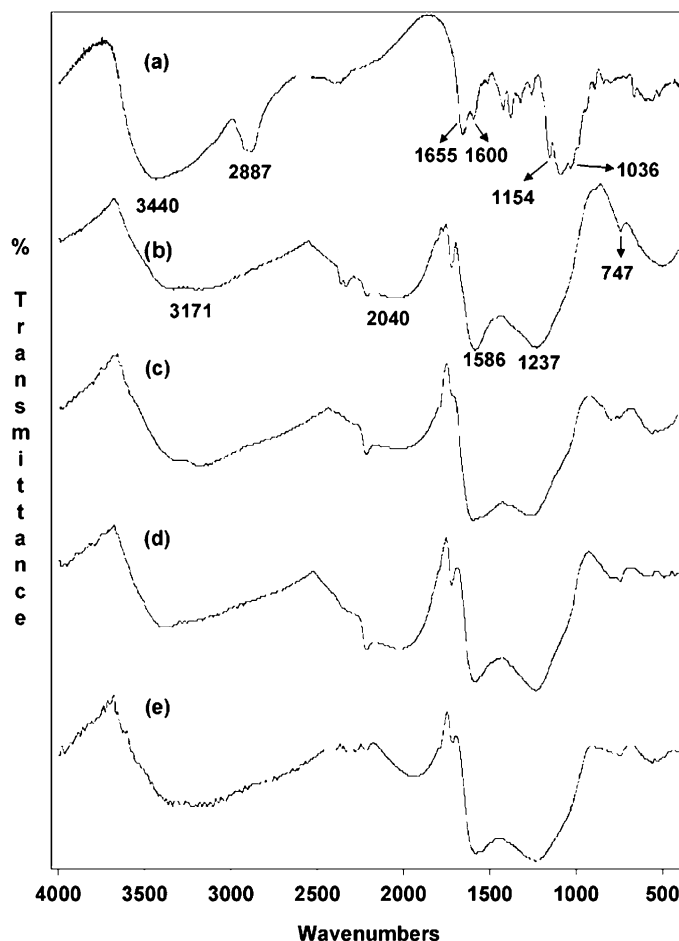


Fig. 2. FTIR spectra of (a) pretreated chitosan powder and products from pretreated chitosan powder oxidized at (b) 300 °C for 60 min, (c) 300 °C for 360 min, (d) 400 °C for 60 min, and (e) 400 °C for 360 min.

IR spectrum of chitosan (Kim, Khor, & Thenmozhiyal, 2000). Although coloration and lowered solubility in aqueous solution were observed, these changes were not accompanied by chemical modifications. FTIR analysis of thermal degradation of chitosan films carried up to 180 °C showed a decrease in absorption due to groups connected with the pyranose ring at 640 and 2920  $\text{cm}^{-1}$ , a decrease in amine group absorption at 1590  $\text{cm}^{-1}$ , and an increase in absorption of carbonyl groups at 1670  $\text{cm}^{-1}$ . The observed changes were interpreted as thermal destruction of the pyranose ring, possible thermal oxidation of polymer and cross-linking of various macroradicals of chains (Mucha, 2000). The IR spectra of residual chitosan from isothermal pyrolysis in the temperature range of 190–240 °C under nitrogen atmosphere shows degradation of the ring together with dehydration (Peniche-Covas, Arguelles-Monal, & San Roman, 1993). Gas chromatography/mass spectroscopy (GC/MS) analysis of volatile compounds generated from pyrolysis of the monomer of chitin, *N*-acetylglucosamine, at 200 °C for 30 min reveals 3-acetamido-5-acetyl furan as the major degradation product and 2-acetyl furan, 3-acetamidofuran, pyrazines, and pyridines as the minor ones (Chen, Wang, & Ho, 1998).

Fig. 2 shows FTIR results of pretreated chitosan and oxidized samples from pretreated chitosan. Pretreated chitosan powder exhibits characteristic chitosan absorption bands of O–H and N–H stretching vibrations of alcohol and amine groups at 3440  $\text{cm}^{-1}$ , C–H stretching vibrations at 2887  $\text{cm}^{-1}$ , N–H bending vibrations at 1655 and 1600  $\text{cm}^{-1}$ , C–H bending vibrations at 1424–1320  $\text{cm}^{-1}$  and C–O stretching vibrations of the pyranose ring at 1154–1036  $\text{cm}^{-1}$ . Pretreated samples oxidized at 300 and 400 °C for 1 and 6 h, respectively, are characterized by the same spectral features. Their O–H and N–H stretching vibrations are diminished compared to chitosan. C–H and C–O vibrations associated with the pyranose ring at 2887 and 1154–1036  $\text{cm}^{-1}$ , respectively, and N–H bending vibrations at 1655 and 1600  $\text{cm}^{-1}$ , are completely lost. These features can be interpreted as the degradation of the chitosan chain and decomposition of the pyranose ring through dehydration and deamination. New peaks appear at 3171, 1586, 1237, and 747  $\text{cm}^{-1}$ , which can be attributed to an aromatic ring formed. Two other new bands at around 2000 and 1723  $\text{cm}^{-1}$  may be due to a cumulated double bond system and some ester groups, respectively. It seems

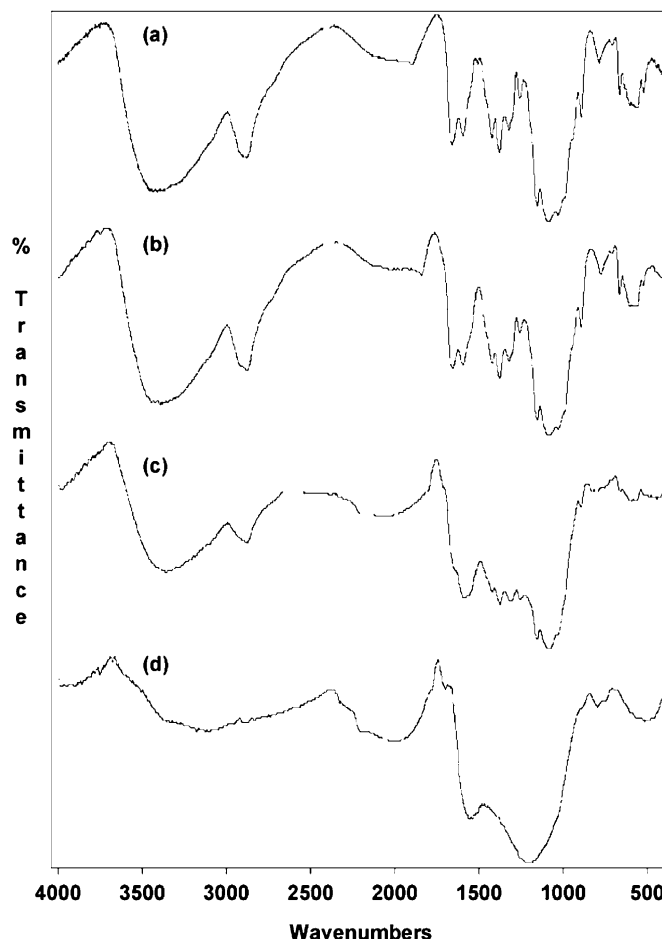


Fig. 3. FTIR spectra of oxidation products obtained within 6 min from pretreated chitosan powder at: (a) 300 °C, (b) 400 °C and from untreated chitosan powder at: (c) 300 °C, and (d) 400 °C.

that prolonged heat treatment of 1 h or longer leads to chemically identical products either at 300 or 400 °C.

The spectra of the oxidation products of pretreated and untreated chitosan obtained within 6 min are compared with each other in Fig. 3. The spectra of the products obtained from pretreated chitosan, Fig. 3a and b, respectively, are identical to each other and to the chitosan spectrum itself, Fig. 2a, showing that pretreatment inhibits oxidation at the initial stage of heat treatment. Oxidation proceeds readily in the absence of pretreatment as reflected in the spectra of products of untreated chitosan. Fig. 3c shows that oxidation begins to occur within 6 min at 300 °C, with dehydration and deamination because the absorption of bands at  $3440\text{ cm}^{-1}$  due to N–H and O–H stretching vibrations diminish and N–H bending vibrations at  $1640$  and  $1600\text{ cm}^{-1}$  are lost. The characteristic new peak of oxidation products at  $1586\text{ cm}^{-1}$ , as explained with reference to Fig. 2, appears to indicate the formation of unsaturated carbon–carbon or carbon–nitrogen bonds. The etheric C–O vibrations of the pyranose ring are still available in the spectrum. At 400 °C, without pretreatment, oxidation is almost complete within 6 min since the spectrum of the product

is identical to those obtained at 1 and 6 h heat treatment as shown in Fig. 2d and e.

Fig. 4 shows the FTIR spectra of oxidized + pyrolyzed and directly pyrolyzed products. Pyrolysis products obtained at 500 °C have a new absorption band at  $1552\text{ cm}^{-1}$ . This can be attributed to a new aromatic ring stretching, indicating further rearrangement of atoms during pyrolysis. The products obtained at 700 °C lack any of the peaks at the  $3000\text{ cm}^{-1}$  region, indicating complete loss of O–H or N–H bonds. C–O stretching of ester groups overlap with in-plane bending of aromatic C–H bonds in the region  $1183\text{--}1046\text{ cm}^{-1}$  for the pyrolyzed products. There is a shift towards shorter wave numbers with higher temperatures and longer heat treatment indicating that the fused aromatic rings formed approach the graphite structure. FTIR spectra of the directly pyrolyzed product after 6 min have absorption bands at  $1861$ ,  $1552$  and  $1090\text{--}1000\text{ cm}^{-1}$  (Fig. 4e and f). The band at  $1552\text{ cm}^{-1}$  shifts to  $1500\text{ cm}^{-1}$  in the case of pyrolysis for 60 min (Fig. 4f).

FTIR spectra of chitosan fiber and pretreated oxidized, oxidized + pyrolyzed and directly pyrolyzed products are compared with each other in Fig. 5a–d, respectively. They show similar spectral features compared to their analogues

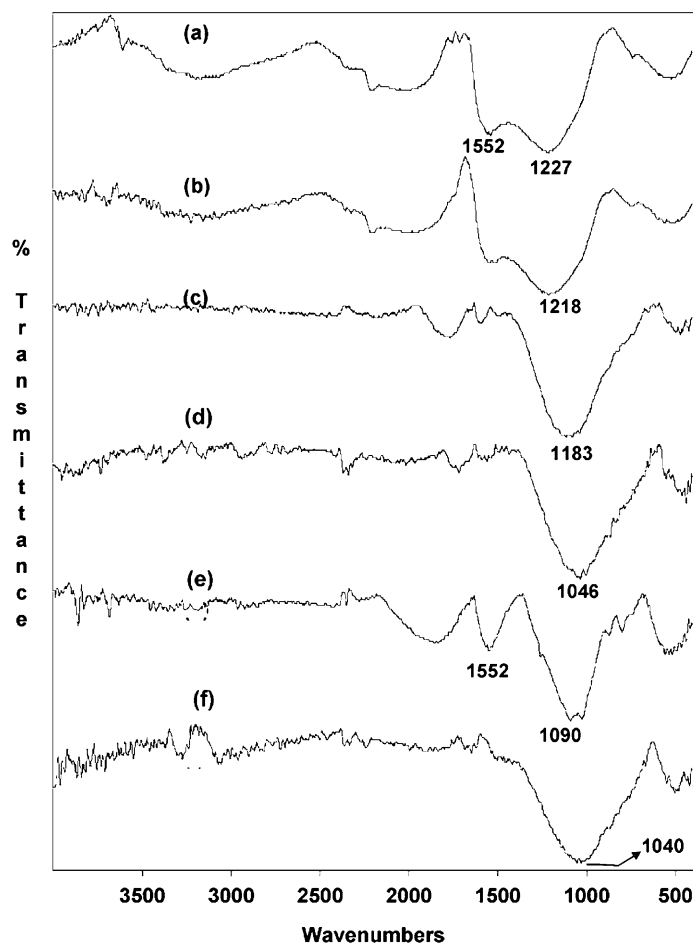


Fig. 4. FTIR spectra of products from pretreated and oxidized chitosan powder pyrolyzed at: (a) 500 °C for 6 min, (b) 500 °C for 60 min, (c) 700 °C for 6 min, (d) 700 °C for 60 min and direct pyrolysis products at: (e) 700 °C for 6 min, and (f) 700 °C for 60 min.

in the powder form. Hence, a similar oxidation and pyrolysis mechanism as described earlier for chitosan powders can be proposed for the fibers as well.

FTIR spectra of oxidized + pyrolyzed or directly pyrolyzed products are very similar to each other (Figs. 4c–f, 5c and d) showing that oxidation might not be a crucial step in obtaining carbon fibers from chitosan.

### 3.2. Mass reduction upon heat treatment

Mass reduction and associated observations during heat treatment provide valuable information on chemical processes. According to TGA of chitosan both in fiber and powder forms, an endothermic reaction occurs in the temperature range 65–111 °C associated with loss of water. Between 300 and 350 °C, an exothermic reaction takes place due to oxidized decomposition. DTA shows that the untreated chitosan powder decomposes at 315 °C, while the decomposition temperature for the untreated fiber is lower (310 °C). Figs. 6 and 7 show the mass reduction during oxidation of chitosan powders and fibers at 300 and 400 °C, respectively. According to ther-

mal degradation studies mentioned above, the mass reduction observed can be linked to dehydration/oxidized decomposition at both temperatures. The mass reduction curves observed, confirm thermal gravimetric analyzes of Peniche-Covas et al. Thus, decomposition starts at around 300 °C, but the rate of decomposition is slower than that at 400 °C. The presence of  $\text{NH}_4\text{Cl}$  in the pretreated powders seems to delay the reaction during the first 10 min both according to mass reduction, colors, and FTIR spectra of the reacted powders. After 5 and 10 min of oxidation, the powders with no pretreatment were all black in color at 400 and 300 °C, respectively, while corresponding pretreated powders had still cream to dark brown color. This delay may be related to the formation of a coating on powders by  $\text{NH}_4\text{Cl}$ , which creates a temporary physical barrier to oxidation. At the later stages of oxidation up to 60 min at both temperatures, pretreatment improves the yield at up to 300 °C and up to 120 min at 400 °C, as clearly indicated by Figs. 6 and 7. The mass change behavior and final yields of fibers and powders are very similar with a final yield of ~30 wt% for untreated chitosan at 300 °C and ~2% for all samples at 400 °C.

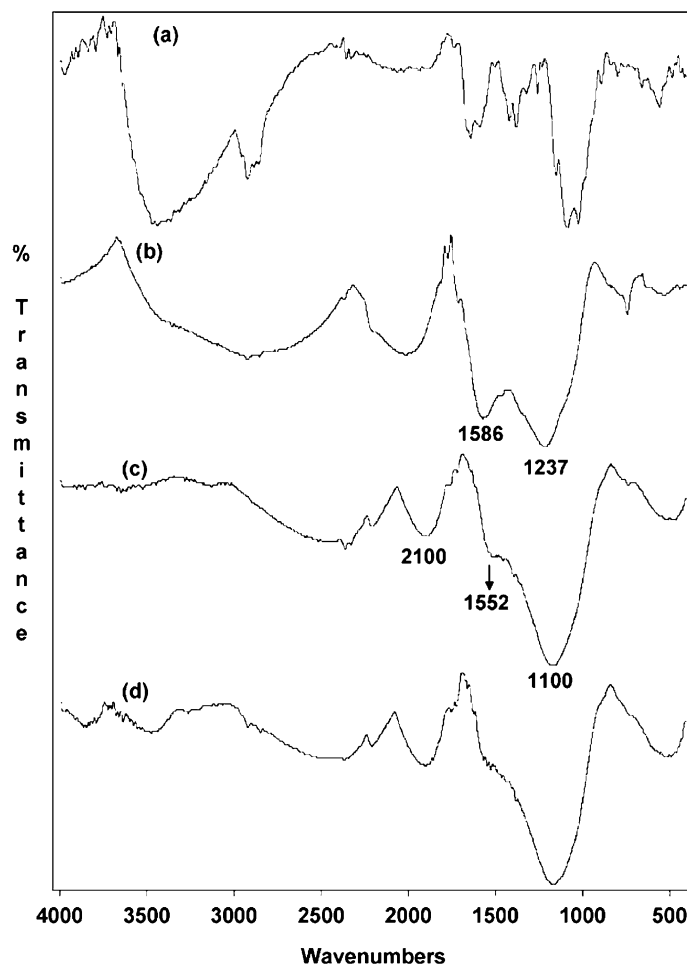


Fig. 5. FTIR spectra of: (a) untreated chitosan fiber, (b) pretreated fiber oxidized at 300 °C for 360 min, (c) pretreated and oxidized fiber pyrolyzed at 500 °C for 6 min, and (d) pretreated fiber directly pyrolyzed at 500 °C for 6 min.

### 3.3. Elemental analysis

Elemental analysis results and % carbon yields of chitosan, oxidized, oxidized + pyrolyzed, and directly pyrolyzed samples are shown in Tables 3 and 4, respectively. A higher pyrolysis temperature and longer heat treatment increases the carbon content of the products. Pretreatment with  $\text{NH}_4\text{Cl}$  seems to increase the carbon content and decrease the nitrogen and oxygen contents of oxidized + pyrolyzed products considerably. Although pretreatment with  $\text{NH}_4\text{Cl}$  delays oxidation of chitosan, it has a favorable effect on the ultimate carbon contents of the products. Since  $\text{NH}_4\text{Cl}$  has a weakly acidic character, chitosan swells in  $\text{NH}_4\text{Cl}$  solution. Hence, in addition to distortion of the crystalline structure, pretreated chitosan has a larger surface area than the untreated one, making it more vulnerable to thermal rearrangement reactions. A similar behavior was observed during thermal treatment of untreated and pretreated cotton linters. Mercerized cotton linter (i.e. cotton linter swollen in  $\text{NaOH}$ ) had a smaller decomposition rate constant and a smaller % weight loss than untreated cotton linter upon heat treatment (Nada,

Kamel, & El-Sakhany, 2000). It seems that the type of interaction, physical or chemical, that takes place between the polymer and the substance used for pretreatment affects the oxidation rate. For example, when an acidic pretreatment bath such as dilute phosphoric acid, instead of basic  $\text{NaOH}$ , is used for cellulose, in addition to acid catalyzed depolymerization, dehydration of the glucopyranose units of cellulose takes place giving rise to levoglucosenone (Dobele, Rossinskaja, Telysheva, Meier, & Faix, 1999) resulting in higher oxidation rates and higher % carbon yield values. Pretreatment of rayon fibers with ammonium chloride solution is known to improve oxidation rate and carbon yield similar to phosphoric acid treatment. On the other hand, pretreatment of chitosan with ammonium chloride which is a weakly acidic bath, does not lead to any chemical change on chitosan which would increase the rate of oxidation or pyrolysis. The best carbon yield obtained from chitosan powder was around 21% both in the case of oxidized + pyrolyzed and in directly pyrolyzed samples. This is higher than that obtained with rayon fibers, namely 15% (Lovell, 1986). Pretreatment consistently improved the carbon yield, except for oxidized

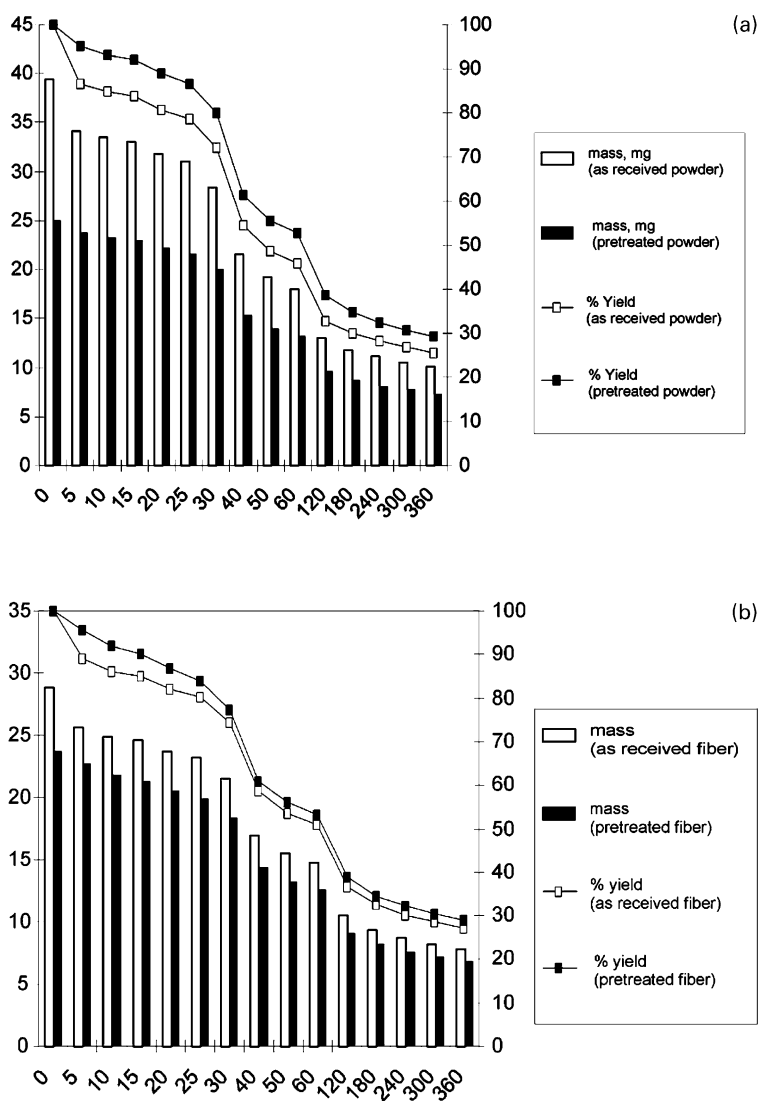


Fig. 6. Mass reduction and % yield (of initial sample mass) during oxidation treatment of chitosan powders and fibers at 300 °C: (a) without pretreatment and (b) pretreated with  $\text{NH}_4\text{Cl}$ .

Table 3  
Elemental analysis results of selected samples

Heat treatment	Experiment no.	Initial powder	1	2	3	4	5	6	7	8
Chitosan powder	% C	40.09								
	% H	6.90								
	% N	6.91								
Oxidation (powder)	% C		56.25	55.78			53.04	52.98		
	% H		2.25	6.18			1.71	1.58		
	% N		13.19	11.91			17.14	16.90		
Pyrolysis (oxidised powder)	% C		54.04	62.46	58.70	64.63	58.47	73.11	61.47	69.92
	% H		1.64	2.38	1.64	2.47	1.47	1.47	1.40	1.37
	% N		19.77	14.28	19.77	15.54	19.70	13.88	17.09	10.96
Pyrolysis (chitosan powder)	% C						74.74		76.22	
	% H						1.79		1.43	
	% N						9.00		7.72	



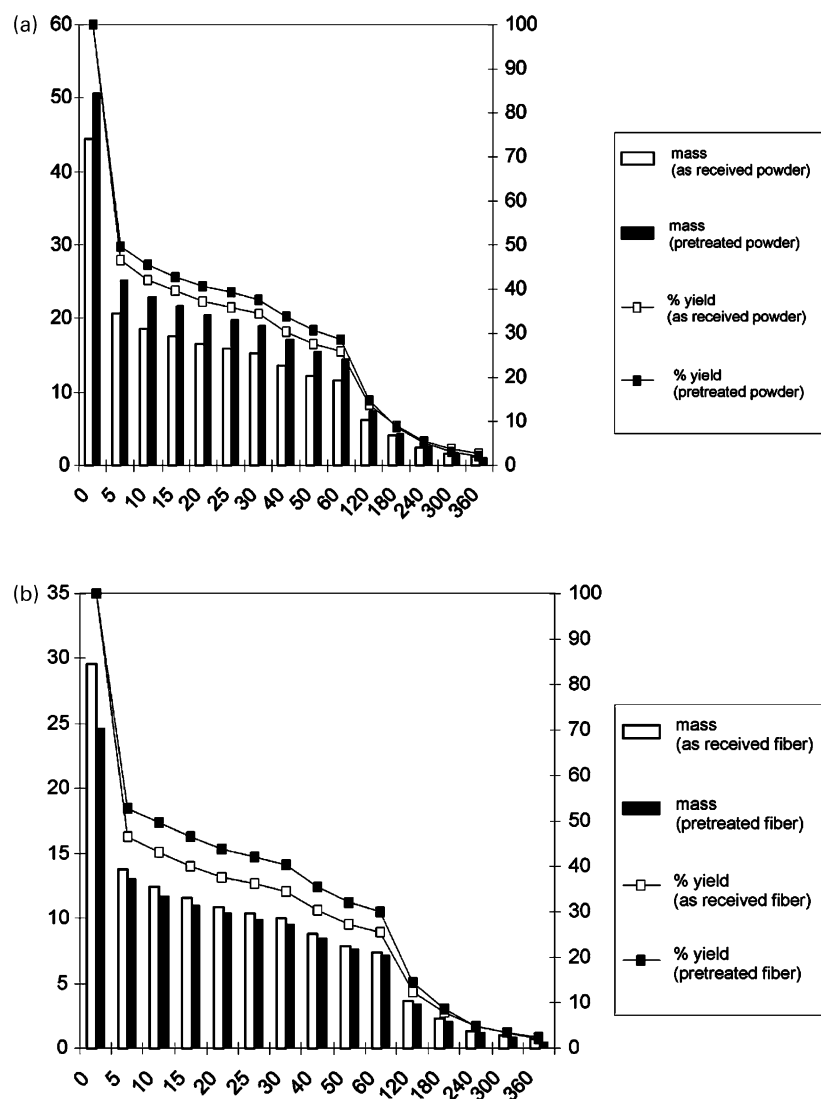


Fig. 7. Mass reduction and % yield (of initial sample mass) during oxidation treatment of chitosan powders and fibers at 400 °C: (a) without pretreatment and (b) pretreated with  $\text{NH}_4\text{Cl}$ .

samples 7 and 8 (Table 4) which have approximately equal C yield values. The oxidation treatment seems to have no identifiable effect on the C yield under the present test conditions.

### 3.4. XRD analysis

XRD analysis was conducted to compare the crystallinity of

chitosan in powder and fiber form as this may affect the conversion rate during pyrolysis. Both XRD patterns are shown in Fig. 8. The main crystalline peak occurred at  $20^\circ$  with an amorphous hump at around  $10^\circ$ . The crystallinity of as received chitosan powders and fibers were calculated to be in the same range and approximately 45%, according to the method of Hermans and Weidinger (Hermans & Weidinger, 1949).

Table 4  
Carbon yields upon heat treatment

Heat treatment	Experiment no.	1	2	3	4	5	6	7	8
Oxidation (powder)	% C assay	56.25	55.78			53.04	52.98		
	% C yield	19.33	21.69			6.27	1.58		
Pyrolysis (oxidised powder)	% C assay	54.04	62.46	58.70	64.63	58.47	73.11	61.46	69.92
	% C yield	15.18	21.46	11.52	13.01	8.57	1.47	3.73	3.45
Pyrolysis (chitosan powder)	% C assay					74.74		76.22	
	% C yield					21.43		21.64	

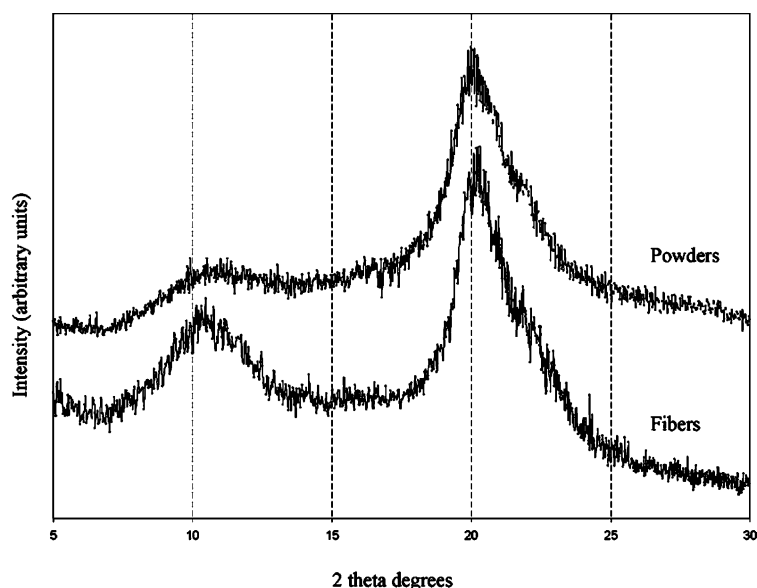


Fig. 8. XRD pattern of as received chitosan powders and fibers.

### 3.5. Mechanical properties

The tensile strengths of fiber bundles were measured using the set-up shown in Fig. 1. During the gluing and alignment stages of fibers, it was observed that the heat treated fibers were more fragile compared to as received chitosan fibers. This was especially identifiable in the case of straining the fibers in directions lying outside the fiber axis, upon which immediate fracture occurs. Even very small strains could result in the destruction of the heat treated samples, while as received fibers can tolerate such small strains. The average tensile strength calculated from bundles with more than 20 fibers for as received chitosan fibers was 403 MPa. After the oxidation treatment, this value fell to 13.5 MPa. However, direct pyrolysis without pretreatment increased the average tensile strength to as high as 591 MPa. This value is significantly lower than the tensile strength of industrially available carbon fibers, ranging between 2000 and 7000 MPa (Savage, 1993), but such high values are obtained upon pyrolysis at much higher temperatures, and in many cases, by stretching the fibers during heat treatment. Further study to analyze the effect of higher temperature pyrolysis on the mechanical properties of chitosan-derived carbon fibers would be valuable.

## 4. Conclusion

FTIR and elemental analysis results show that the pyrolysis of chitosan fibers at relatively low temperatures is an effective method for obtaining C-fibers. The mechanism for the conversion of chitosan to carbon during oxidation, suggested by FTIR analysis, is one where degradation takes place together with decomposition of the pyranose ring with partial dehydration and

deamination. Some ester formation and aromatization occurs at the oxidation stage. During pyrolysis, dehydration and deamination are completed accompanied by fusion of the aromatic rings formed. Pretreatment of fibers with  $\text{NH}_4\text{Cl}$  improves the C yield. However, the oxidation step seems to have no beneficial effect, unlike the case for rayon-derived C fibers. Optimum results in terms of C yield and tensile strength were obtained by direct pyrolysis of chitosan at 700 °C. A higher C yield is obtained with chitosan fibers compared to rayon fibers (>20 vs. 15%, respectively) even at relatively low pyrolysis temperatures. Additional experiments related to the effect of different pretreatment agents, higher temperatures and stretching of fibers during pyrolysis on the C yield and mechanical properties of chitosan-derived C-fibers would be beneficial as future research areas.

## Acknowledgements

M.B. thanks Prof. Richard Brow (Ceramic Engineering Department, University of Missouri-Rolla (UMR)) for his kind support for XRD and DTA analyses and Mr Eric Bohannon (Materials Research Center, UMR) for his help and valuable discussions regarding XRD data analysis.

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