

Effect of $(\text{NH}_4)_2\text{SO}_4$ Concentration on the Pyrolysis Properties of Rayon Fiber from Bamboo

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$(\text{NH}_4)_2\text{SO}_4$ solution was employed to pre-treat regenerated cellulose fiber (from bamboo) using an ultrasonic method, and then the material was heat-treated at 250 °C. Scanning electron microscopy revealed that erosion and cracks of the fiber surface increased after being impregnated with $(\text{NH}_4)_2\text{SO}_4$ combined with ultrasonic pretreatment. There was a small change in the intensity and the position of some peaks in the Fourier transform infrared spectra, and in the heat treatment, partial pyrolysis of the cellulose occurred. The data showed that for the cellulose fiber pretreated with 5 wt% $(\text{NH}_4)_2\text{SO}_4$ the decomposition temperature shifted to the lower side (252 °C), and the decomposition range (180 °C to 454 °C) was wider than for the other impregnation fibers and reference. However, the rate of decomposition was different with different concentrations of $(\text{NH}_4)_2\text{SO}_4$. The C content of heat-treated fiber with 5 wt% $(\text{NH}_4)_2\text{SO}_4$ increased to 52%. The above results indicated that the $(\text{NH}_4)_2\text{SO}_4$ was an effective catalyst to pretreat regenerated cellulose fiber in the pathway of pyrolysis.

Keywords: Bamboo cellulose; Regenerated cellulose; Pyrolysis property; TG; FTIR; Elemental analysis

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INTRODUCTION

Carbon fiber, called “black gold” in the industry, offers the highest specific modulus and specific strength among all reinforcing fibers (Tiwari and Bijwe 2014). These features contribute to their high performance in various applications such as reinforced materials, aerospace materials, conductive material, *etc.* The main raw material for manufacturing carbon fiber is polyacrylonitrile (PAN), which is a synthetic petroleum-based polymer. Other raw materials, such as coal- and petroleum-derived pitches, lignin, and regenerated cellulose (Rayon), could also be used for manufacturing carbon fiber. Some differences in final properties can be expected with different manufacturing methods. However, the production of PAN as a precursor accounts for approximately half of the total production cost. The high costs of PAN carbon fiber have increased interest in searching for alternative fiber precursors, for which rayon fiber is a possible material. Currently, Rayon-based carbon fiber is widely used in aerospace and the aeronautics field due to its high thermal stability, elongation at rupture, and good biological compatibility.

China is rich in bamboo material resources, and it is important to explore the new, high value added utilized method of bamboo through chemical processes. Bamboo rayon fibers have been seen as a new promising environmental fabric material and have gained acceptance for manufacturing and processing of textiles because of their good strength,

wear resistance, flexibility, non-toxicity, biocompatibility, and lack of harm to the biological environment (Teli and Sheikh 2013).

For producing high-strength carbon fibers from cellulose fibers, thermo-oxidation or pyrolysis is one of the necessary stages and is as important as carbonization. Many workers (Byrne *et al.* 1966; Banyasz *et al.* 2001) have studied cellulose pyrolysis and indicated that its pyrolysis includes at least two pathways with one producing tars/levoglucosan whilst the other forming lighter fragments such as glycoaldehyde and formaldehyde. The formation of char residue in the pyrolysis of rayon fiber could contaminate the fiber surface and even conglomerate the fiber together, which would be adverse to the quality of the carbon fiber formed. Therefore, it is essential to control the initial stage of pyrolysis.

Many studies have found that acid-washing (Dobele *et al.* 2001; Piyali *et al.* 2004) and inorganic ammonium salts (Liu *et al.* 2004) pretreatment could effectively accelerate pyrolysis reactions (Statheropoulos and Kyriakou 2000). Li *et al.* (2007) demonstrated that $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{Cl}/\text{organosilicon}$ was an effective composite catalyst system in the preparation of Rayon-based carbon fibers. Many studies have been focused on thermal degradation of natural (Byrne *et al.* 1966; Boon *et al.* 1994) or artificial (Bacon and Tang 1964) cellulosic fibers. Due to the thermal and mechanical properties of bamboo-derived Rayon fibers being different from wood and cotton-type Rayon fiber, it is necessary to pay attention to the thermal decomposition or pyrolysis of the regenerated cellulose fibers when exploring the new bamboo-derived regenerated cellulose fiber to manufacture the Rayon-based carbon fiber.

Many studies have reported that $(\text{NH}_4)_2\text{SO}_4$ is an effective fire retardant (Kandola and Horrocks 1996; Pappa *et al.* 2006) because it can enhance the first decomposition pathway and consequently increase the amount of char residue, which prevents oxygen from reaching the substrate and insulates the forest fuel surface from high temperatures. In addition, nonflammable gases released by the decomposition of the fire retardant chemicals form a non-flammable gaseous mixture (Statheropoulos and Kyriakou 2000). However, more attention needs to be paid to the char residue and non-flammable gaseous mixture during pyrolysis of materials. For instance, the microstructure of materials and the elemental content, especially the C content, has not been adequately considered. At the base of the present research, $(\text{NH}_4)_2\text{SO}_4$ solution was employed to pretreat the regenerated cellulose fibers in an ultrasonic processor at 70 °C. The work was focused on the effect of the concentration of $(\text{NH}_4)_2\text{SO}_4$ solution on the pyrolysis reaction of cellulose fibers, and the decomposition of the fibers was preliminarily investigated. The surface properties and the change of the chemical structure of fibers before and after pretreatment were studied with SEM and Fourier transform infrared (FTIR) analysis. The change in elemental content of fibers before and after high temperature heat treatment was also studied with elemental analysis.

EXPERIMENTAL

Materials

Rayon fibers, produced from bamboo, were obtained from a factory located in Zhejiang, China. The material, which will be called “cellulose fiber” in this article, had a degree of polymerization of 350 to 380, and contain less than 0.2% ash. In order to

remove the negative effect of the impurities of fiber samples on the latter experiment, the cellulose fiber was washed with warm distilled water and then dried in a vacuum drying oven.

Methods

Preparation of sample

The $(\text{NH}_4)_2\text{SO}_4$ reagent used was of analytical grade (> 99.0%) from Nanjing Chemical Reagents Corp., P. R. China. Firstly, the different concentration with 1%, 5% and 20% w/w of $(\text{NH}_4)_2\text{SO}_4$ solutions were prepared, then the cellulose fibers were impregnated in these $(\text{NH}_4)_2\text{SO}_4$ solutions with the bath ratio 1:30, respectively, and finally put them to the ultrasonic generator with power 500 w for 1 h with temperature 70 °C, followed by overnight vacuum drying.

Heat treatment of the cellulose fiber

The cellulose fibers impregnated with different concentrations of $(\text{NH}_4)_2\text{SO}_4$ solutions were put into the heat treated apparatus. The fibers were heated directly to 100 °C in 10 min, and then elevated temperature to 250 °C in 2 h. Finally, the fibers were heat treated at 250 °C for 30 min.

SEM analysis

To study the effects of impregnation with $(\text{NH}_4)_2\text{SO}_4$ on the morphologies and microstructure of bamboo-derived rayon cellulose fibers, scanning electron microscopy (SEM) analysis with JEOL-35C (Japan) was conducted, and the SEM micrographs of the surfaces of the fibers before and after impregnation with $(\text{NH}_4)_2\text{SO}_4$ were compared.

FTIR analysis

FTIR spectra of cellulose fibers before and after impregnation were recorded with a Nicolet FTIR Spectrometer 360 in 400 to 4000 cm^{-1} . For the preparation of FTIR specimens, the fiber samples were first milled into powder, and then approximately 5 mg of each powder sample was ground and mixed with 200 mg KBr powder uniformly. Moreover, prior to mixing, each fiber sample, as well as KBr, were dried under an infrared lamp for 30 min.

TG analysis

The thermogravimetric analyzer (TGA) Q500 that was used was made by TA Instruments (USA). Weight loss of the cellulose fibers during pyrolysis was measured in the TGA, where the working atmosphere was ultra-high pure argon (99.999%). Approximately 5 mg of sample was heated from room temperature up to 800 °C at the heating rate of 20 °C/min in the pyrolysis experiments. Derivative thermogravimetry (DTG) analysis was used in order to study the characteristic temperature of TGA curves.

Elemental analysis

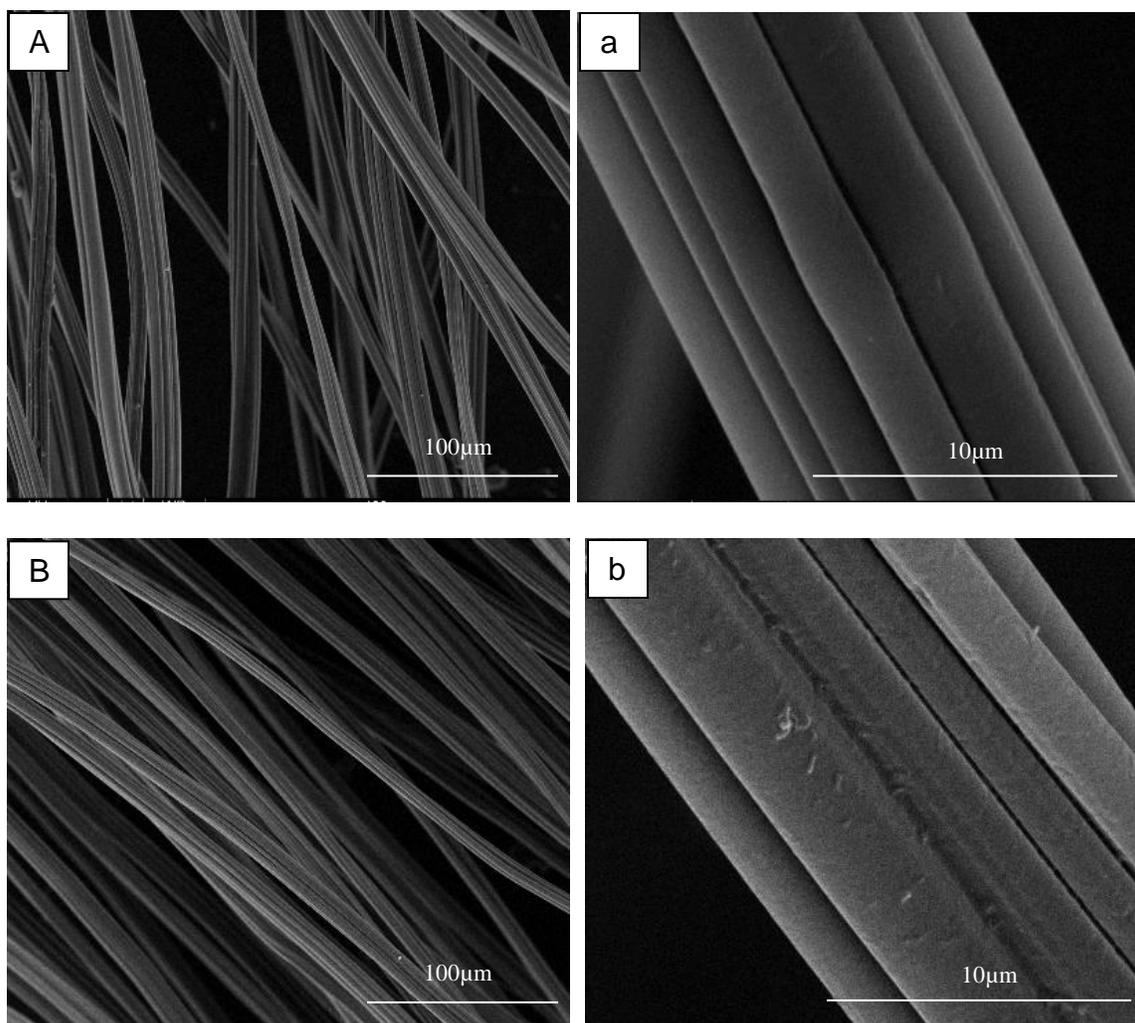
Elemental analysis was carried out using a model Thermo Scientific FLASH 2000 instrument. The carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) contents of the heat-treated fibers were determined directly using the thermal conductivity detector (TCD), and the oxygen (O) content was then obtained by difference.

RESULTS AND DISCUSSION

Microstructure of Bamboo-Derived Rayon Fibers

The microstructure of the cellulose fiber before and after the $(\text{NH}_4)_2\text{SO}_4$ impregnation was characterized by SEM observation. Figure 1(A, a) shows the microstructure of regenerated cellulose fiber that had not been impregnated (designated as reference), and Fig. 1(B, b to D, d) shows the surface structure of the cellulose fiber pretreated with different concentration of $(\text{NH}_4)_2\text{SO}_4$.

As can be seen from Fig. 1, the morphology of cellulose fibers were changed during pretreatment. There are many grooves on the original regenerated cellulose fiber and the surface of fiber was smooth and compact (Fig. 1 a). Some defects and a large number of small dents on the fiber surface became distinct (Fig. 1 b, c, and d), and the degree of defects increased with the increasing concentration of $(\text{NH}_4)_2\text{SO}_4$. It is clear that pretreatment would increase the probability of the permeability of the fiber to chemical agents. This means that the molecular water and NH_4^+ ions could diffuse into the amorphous regions and some surface area of crystalline regions of the fiber associated with more hydrogen bonds.



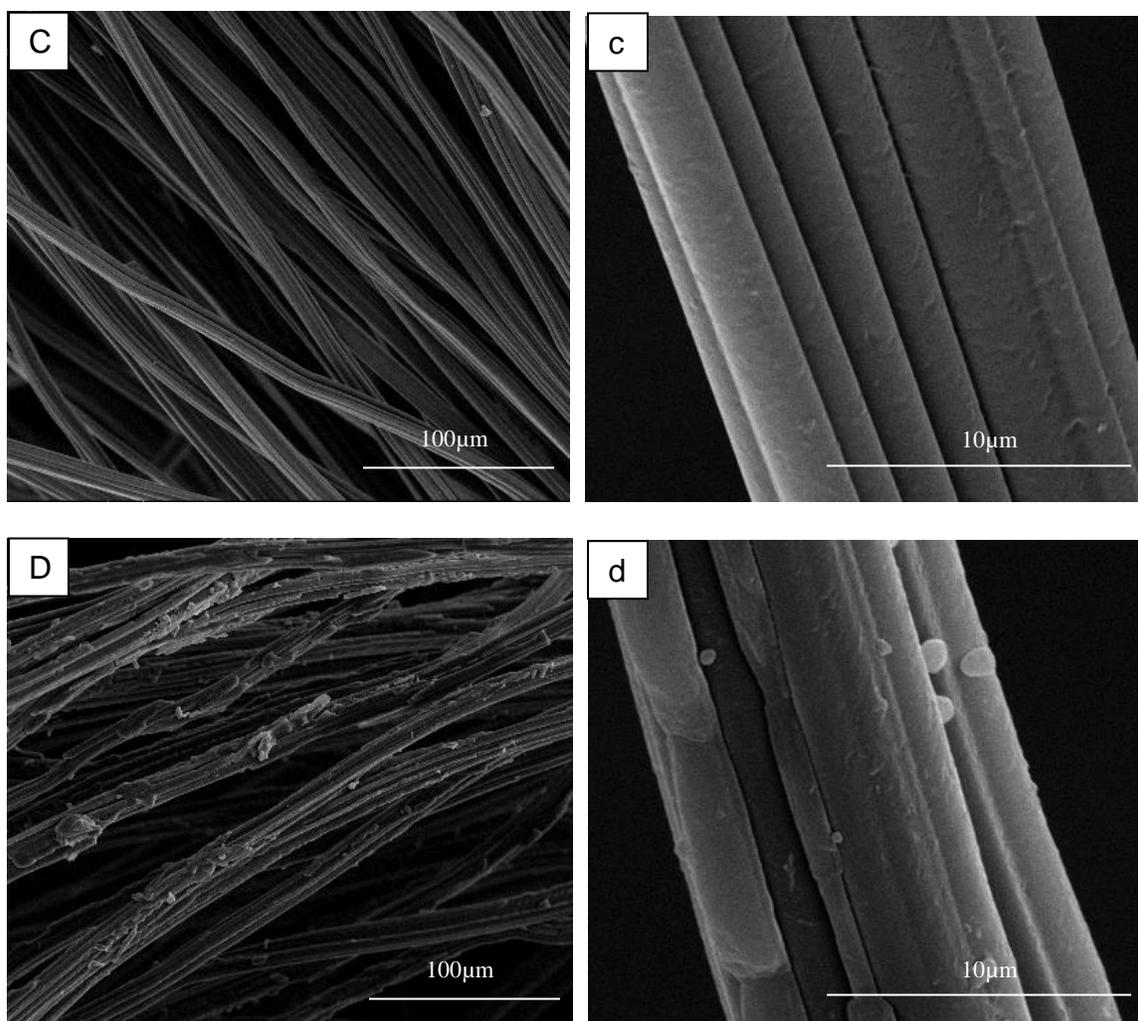


Fig. 1. SEM of regenerated cellulose fiber before and after chemical pretreatment (A,a: reference; B,b:1% $(\text{NH}_4)_2\text{SO}_4$ impregnation; C,c: 5% $(\text{NH}_4)_2\text{SO}_4$ impregnation; D,d: 20% $(\text{NH}_4)_2\text{SO}_4$ impregnation)

Tang *et al.* (2014) found that asymmetric cavitation, involving the collapse of bubbles and taking place at the fiber-water interface during ultrasonic treatment, could lead to the erosion of the fiber surface (Wang *et al.* 2007). Moreover, the erosion and dents produced by pretreatment process would be increased in amorphous regions of cellulose more than the crystalline regions. On the other hand, due to the participation of hydrogen bond interactions, the NH_4^+ ions would penetrate into the super-molecule structure of the regenerated cellulose fibers. Therefore, the chemical agent adhering to the surface of fiber could not be cleaned from the surface and the pore structure of the fiber (Fig.1 D, d). Thus, the part of $(\text{NH}_4)_2\text{SO}_4$ would remain on the fiber and participate the pyrolysis reaction.

FTIR Analysis

FTIR spectra in the 4000 to 450 cm^{-1} region are shown for the regenerated cellulose fiber treated by $(\text{NH}_4)_2\text{SO}_4$ at 70 °C (Fig. 2). Typical FTIR spectra of fibers pretreated with different concentration $(\text{NH}_4)_2\text{SO}_4$ showed different vibrations (with

assignments in Table 1). Some characteristic bands related to the chemical changes are the CH stretching at 2900 cm^{-1} , the CH deformation vibration at 1375 cm^{-1} , the band at 897 cm^{-1} assigned as C-O-C stretching at the β -(1,4)-glycosidic linkage (Proniewicz *et al.* 2001), and the C-OH out of plane bending mode at 668 cm^{-1} (Richardson and Gorton 2003; Schwanninger *et al.* 2004).

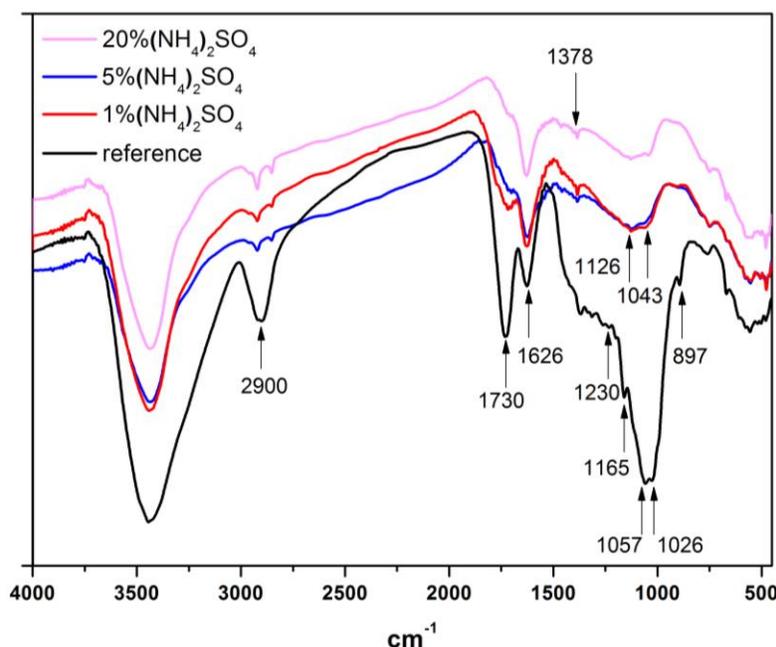


Fig. 2. FTIR spectra (4000 to 450 cm^{-1}) of cellulose fiber and its impregnated with $(\text{NH}_4)_2\text{SO}_4$

Table 1. IR Assignments of the Main Vibrations in the FTIR Spectra

Vibrations (cm^{-1})	Band origin, short comments
2918,2850	C-H stretch in methyl and methylene groups
1730	C=O stretch in unconjugated ketones, carbonyls and in ester groups
1620	originating from the carbonyl groups
1370	aliphatic C-H stretch in CH ₃
1230	C-C plus C-O plus C=O stretch
1165	Anti-symmetrical bridge C-O-C stretching, glycosidic linkages
1056,1026	C-O stretch
897	β -Linkage of cellulose

As can be seen from Fig. 2, the CH stretching mode at 2900 cm^{-1} was divided into two bands at wavenumber 2920 cm^{-1} and 2850 cm^{-1} after impregnation with $(\text{NH}_4)_2\text{SO}_4$. The two bands can be assigned to CH₂ asymmetrical and symmetrical stretching, respectively (Abidi *et al.* 2010), and absorbance of the band at 2920 cm^{-1} and 2850 cm^{-1} increased with increasing concentration of $(\text{NH}_4)_2\text{SO}_4$. This is because the sulfate anion seems to have played the role of an acidic catalyst combined with ultrasonic treatment at

70 °C to promote partial hydrolysis of the fiber's cellulose in this environment. The spectra show the emergence of bands at 1730 cm^{-1} , which can be attributed to C=O stretching; these decreased and even disappeared after pretreatment by $(\text{NH}_4)_2\text{SO}_4$.

It is clear that the broad band at 1620 cm^{-1} originated from carbonyl groups. The bands at 1370 cm^{-1} were assigned to CH bending. After impregnation they became decreased and shifted to a higher wavenumber by about 8 cm^{-1} (reaching 1378 cm^{-1}). The band at 1500 cm^{-1} to 1375 cm^{-1} became divided into some very small bands after impregnation. There was a complex absorption band between 1500 cm^{-1} and 1375 cm^{-1} with a maximum near 1440 cm^{-1} attributed to $-\text{CH}_2$ bending. The peak around 1378 cm^{-1} could be attributed to CH bending vibrations in cellulose, and no obvious difference could be found.

When the cellulose fiber was pretreated with $(\text{NH}_4)_2\text{SO}_4$ solutions in ultrasonic reactor at 70 °C, partial hydrolysis could have occurred and amorphous cellulose would be formed. The pretreatment temperature at 70 °C in a weak acid environment would cause the molecular rupture and changes in configuration. Also, some bands between 1300 and 1100 cm^{-1} , with a maximum near 1230 cm^{-1} , which corresponded to aliphatic C-C and C-O stretching, were almost absent after impregnation. The peak near 1165 cm^{-1} signifies glycosidic linkages and C-O or C-O-C stretching vibrations (Kumar *et al.* 2010). It was observed that 1159 cm^{-1} and 1057 cm^{-1} absorbances related to ring stretching were shifted to a lower wavenumber at 1126 cm^{-1} and 1043 cm^{-1} and decreased in their adsorption intensity, indicating that the pyranose ring was altered after pretreatment. The chemical agent was prone to penetrate to the fiber after impregnation because of the increasing of surface area of cellulose fiber, and the cellulose would undergo pyrolysis in the weakly acidic environment. The disappearance of the 897 cm^{-1} vibration indicates that the cellulose molecular structure was destroyed after impregnation with $(\text{NH}_4)_2\text{SO}_4$ during the ultrasonic process; that is, the partial pyrolysis of cellulose of the fiber at 70 °C would have occurred.

Pyrolysis of Bamboo-derived Rayon Fiber

TGA and the first derivative thermogravimetric (DTG) curves of the cellulose fibers impregnated with $(\text{NH}_4)_2\text{SO}_4$ and reference are shown in Figs. 3 and 4.

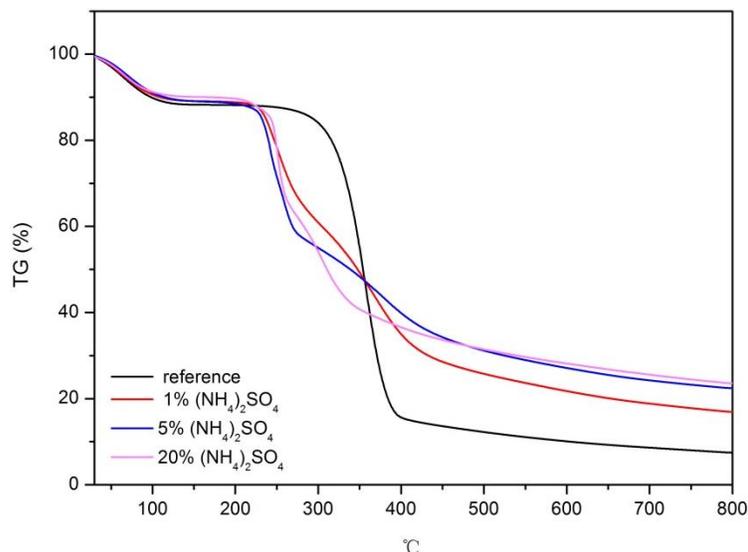


Fig. 3. TG curves of regenerated cellulose fiber before and after impregnation

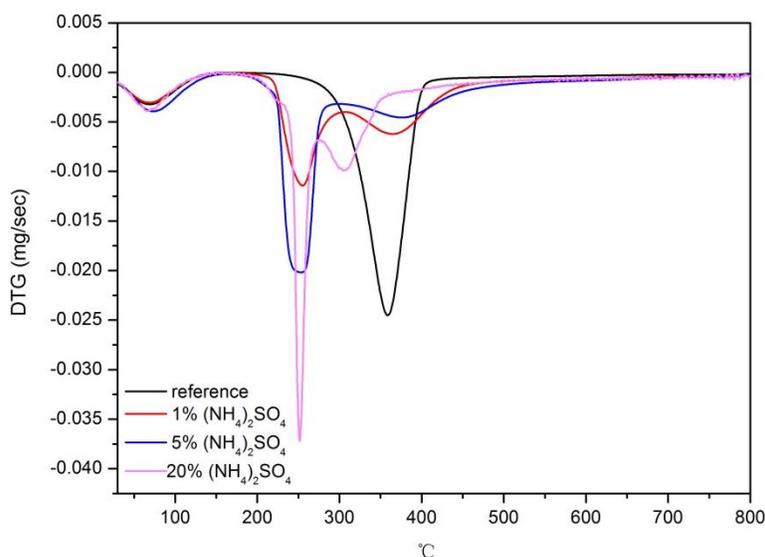


Fig. 4. DTG curves of regenerated cellulose fiber before and after impregnation

As can be seen in the figures, there was some difference in the TG/DTG curves between fibers before and after impregnation with $(\text{NH}_4)_2\text{SO}_4$. In the low temperature range lower than 135°C mainly physically adsorbed water evaporates.

The processes of depolymerization would be taking place to an increasing extent with increasing temperature. The decomposition proceeds in two competing pathways, and rearrangement would occur between 200°C and 500°C , resulting in a considerable mass loss. Meanwhile, char residue and liquid and gaseous compounds would be generated. As the temperature rose higher than 500°C , the structure of the semi-products generated in the previous stage started to change and finally led to the formation of products with high carbon content.

The shoulder of the TG curve of cellulose fiber after impregnation appeared in advance compared to the reference (Fig. 3), and correspondingly, the decomposition temperature presented in the DTG curve shifted to the lower side and the formation of char residue was increased due to the enhancement of the first decomposition pathway when the cellulose fiber was impregnated with $(\text{NH}_4)_2\text{SO}_4$ solution.

It is known that the thermally decomposed products of $(\text{NH}_4)_2\text{SO}_4$, especially H_2SO_4 , are active components that could promote the thermal decomposition of cellulose (Statheropoulos and Kyriakou 2000). The decomposition of the reference takes place over the 255°C to 428°C temperature range and with a mass loss of about 73%. When the cellulose fiber was impregnated with 1%, 5% and 20% $(\text{NH}_4)_2\text{SO}_4$, the decomposition ranges were from 212 to 446°C , 187°C to 490°C , and 180°C to 454°C , respectively, and the mass loss was about 57% or so. It has been observed that thermal decomposed of $(\text{NH}_4)_2\text{SO}_4$ will bring about the active production of H_2SO_4 , which would accelerate the reaction (Statheropoulos and Kyriakou 2000). The maximum rate of the decomposition reaction of cellulose fiber after impregnation was less than the reference, which decreased gradually with increasing concentration of the $(\text{NH}_4)_2\text{SO}_4$. However, there was no significant difference between cellulose fiber impregnated with 5% and 20% $(\text{NH}_4)_2\text{SO}_4$.

It was observed that the maximum rate of decomposition of cellulose fiber was situated at 364°C . As can be seen from pyrolysis of rayon fiber, wood-derived rayon

fiber showed that the maximum rate of weight loss is at 335 °C, corresponding to a weight loss of around 84% (Liu *et al.* 2004). The cotton-derived rayon fibers showed a starting pyrolysis temperature was around 280 °C to 400 °C with a sharp weight loss at 319 °C (Li *et al.* 2007). Kumar (2010) study pyrolysis of the bamboo fiber (natural fiber) and bamboo fiber/LLDPE, and two steps were observed in the decomposition reaction because of the LLDPE. The one step of decomposition was in the range 300 to 350°C was attributed to thermal degradation of part of cellulose and lignin, and the char yield was 1.25%. In case of bamboo fiber reinforced LLDPE composites, the decomposition in the first mass loss step shifted to the high temperature and the second step can be assigned for the decomposition of LLDPE. Therefore, the diversities of fiber resources employed would lead to the differences in the outcomes of pyrolysis. The DTG curve of regenerated cellulose fiber impregnated with (NH₄)₂SO₄ presented two maxima (Fig. 2), one occurring at a temperature of 254 °C and the other at 368 °C after impregnated with 1% (NH₄)₂SO₄; one was situated at temperature of 252 °C and the other at 388 °C with 5% (NH₄)₂SO₄ impregnation; one attained at a temperature of 251 °C and the other at 307 °C after with 20% (NH₄)₂SO₄ impregnation. These findings indicate two steps in the decomposition reaction. This result is the same as what was found by Liu *et al.* (2004). This probably corresponding to dehydration of the levoglucosan polymerization (Bai *et al.* 2013). On the other hand, the produced char residue from pyrolysis of cellulose fiber was about 9.4% at 800 °C, and the value increased to 27.86% after pyrolysis of cellulose fiber with impregnation of 20% (NH₄)₂SO₄. There was no benefit of adding (NH₄)₂SO₄ solution during formation of char residue when the concentration of (NH₄)₂SO₄ reached 5%.

Elemental Analysis

Elemental analysis data of cellulose fibers impregnated with (NH₄)₂SO₄ solution and the reference after heat treated at 250 °C are shown in Table 2.

Table 2. Elemental Composition of Regenerated Cellulose Fiber Impregnated with Different wt% (NH₄)₂SO₄ and the Reference

Specimens	C (wt.%)	H (wt.%)	O (wt.%)	S (wt.%)	N (wt.%)
The reference	44	6.53	49.31	0.072	0.089
1% (NH ₄) ₂ SO ₄	46	2.90	50.52	0.069	0.51
5% (NH ₄) ₂ SO ₄	52	2.40	42.00	0.38	3.22
20% (NH ₄) ₂ SO ₄	54	2.10	31.13	2.62	10.15

Compared with the reference with 44% carbon content, the carbon content in the sample of cellulose fibers impregnated with 1% (NH₄)₂SO₄, 5% (NH₄)₂SO₄, and 20% (NH₄)₂SO₄ increased to 46%, 49%, and 54%, respectively. The carbon content increased with increasing concentration of (NH₄)₂SO₄. It should be noted that the reference contained a higher content of oxygen atom (49.31%) indicating the presence of some oxygen containing groups on the fiber surface, such as oxygen atoms in the aldehyde and hydroxylic groups of the cellulose molecules of the cellulose fiber. While the content of

all the hydrogen and oxygen in the three specimens treated with $(\text{NH}_4)_2\text{SO}_4$ decreased, the contents decreased with increasing concentration of the impregnation solution. When cellulose fibers were treated with 20% $(\text{NH}_4)_2\text{SO}_4$, the oxygen and hydrogen content decreased by 36.9% and 67.8%. In contrast, the three samples treated with $(\text{NH}_4)_2\text{SO}_4$ contained more nitrogen and sulfur content than the reference. One reason is that the $(\text{NH}_4)_2\text{SO}_4$ possessed nitrogen and sulfur atoms, while the unit of cellulose in the regenerated cellulose fiber had relatively high amounts of hydrogen and oxygen atoms; therefore, the amounts of nitrogen and sulfur were increased relatively. Data for the cellulose fiber impregnated with $(\text{NH}_4)_2\text{SO}_4$ indicate that the dehydration reaction in the cellulose would take place after heat treatment. That is, primary hydroxyl group of the cellulose is eliminated because of the thermal scission of glycosidic bonds at high temperature heat treatment.

Mamleev *et al.* (2009) proposed a cellulose thermochemical conversion/pyrolysis scheme that stated the initial thermal degradation pathway was mainly *via* intermolecular transglycosylation reactions within the glucose monomers of cellulose, and levoglucosan and levoglucosenone were produced. Statheropoulos and Kyriakou (2000) revealed that the application of the $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ on rayon fiber would decrease the level of levoglucosan and relatively increase the levoglucosenone, and consequently increase the amount of char residue. On the other hand, cellulose materials treated with various inorganic compounds have been reported to catalyze the dehydration reaction in intermolecular interaction (Sekiguchi and Shafizadeh 1984; Venkateswaran *et al.* 1990) as a result of the pyrolysis of the C-O and C-C. Thus, the evolution of H_2O and CO_2 is increased, and therefore the oxygen and hydrogen were decreased after impregnated with $(\text{NH}_4)_2\text{SO}_4$. Furthermore, the active sites of SO_4^{2-} may promote cellulose dehydration and inhibit its rapid degradation, increasing the yield of levoglucosenone.

CONCLUSIONS

1. SEM analysis revealed that there was some erosion and dents on the surface of bamboo-derived regenerated cellulose fiber after $(\text{NH}_4)_2\text{SO}_4$ impregnation; this also increased the opportunity for $(\text{NH}_4)_2\text{SO}_4$ to penetrate into the cellulose fiber.
2. The FTIR results showed that the vibrations observed at 2920, 2850, 1730, 1378, 1230, 1057, and 897 cm^{-1} are useful indicators of partial pyrolysis of the cellulose of the fiber. $(\text{NH}_4)_2\text{SO}_4$ can effectively accelerate the decomposition of the regenerated cellulose fiber.
3. The impregnation of the cellulosic fibers with $(\text{NH}_4)_2\text{SO}_4$ was able to shift the decomposition temperature to the lower side, about 300 °C, and decrease the maximum rate of weight loss, while increasing the char residue formed. The TG/DTG analysis showed that the pyrolysis temperature of the fiber decreased from 364 °C to 252 °C after impregnation with 5 wt% $(\text{NH}_4)_2\text{SO}_4$.
4. The C content of the regenerated cellulose fiber impregnated with $(\text{NH}_4)_2\text{SO}_4$ were increased. The C content of the regenerated cellulose fiber impregnated with 5 wt% $(\text{NH}_4)_2\text{SO}_4$ was 52%. The N and S contents increased because of adding of $(\text{NH}_4)_2\text{SO}_4$. The results indicated that the SO_4^{2-} in $(\text{NH}_4)_2\text{SO}_4$ would promote dehydration of cellulose of the fiber in the pathway of pyrolysis.

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REFERENCES CITED

- Abidi, N., Cabrales, L., and Hequet, E. (2010). "Fourier transform infrared spectroscopic approach to the study of the secondary cell wall development in cotton fiber," *Cellulose* 17(2), 309-320. DOI: 10.1007/s10570-009-9366-1
- Bacon, R., and Tang, M. (1964). "Carbonization of cellulose fibers," *Carbon* 2, 211-215. DOI: 10.1016/0008-6223(64)90035-1
- Bai, X. L., Johnston, P., and Brown, R. C. (2013). "An experimental study of the competing processes of evaporation and polymerization of levoglucosan in cellulose pyrolysis," *Journal of Analytical and Applied Pyrolysis* 99,130-136. DOI: 10.1016/j.jaap.2012.10.012
- Banyasz, J. L., Li, S., Lyons-Hart, J., and Shafer, K. H. (2001a). "Gas evolution and the mechanism of cellulose pyrolysis," *Fuel* 80(12), 1757-1763. DOI: 10.1016/S0016-2361(01)00060-6
- Banyasz, J. L., Li, S., Lyons-Hart, J. L., and Shafer, K. H. (2001b). "Cellulose pyrolysis: The kinetics of hydroxyacetaldehyde evolution," *J. Anal. Appl. Pyrolysis* 57(2), 223-248. DOI: 10.1016/S0165-2370(00)00135-2
- Boon, J. J., Pastorova, I., Botto, R. E., and Arisz, P. W. (1994). "Cellulose char structure: A combined analytical Py-GC-MS, FTIR, and NMR study," *Carbohydr. Res.* 262, 27-47. DOI: 10.1016/0008-6215(94)84003-2
- Byrne, G. A., Gardiner, D., and Holmes, F. H. (1966). "The pyrolysis of cellulose and the action of flame-retardants," *J. Appl. Chem.* 16 (3), 81-88. DOI: 10.1002/jctb.5010160303
- Dobele, G., Meier, D., Faix, O., Radtke, S., Rossinskaja, G., and Telysheva, G. (2001). "Volatile products of catalytic flash pyrolysis of celluloses," *J. Anal. Appl. Pyrolysis* 58-59, 453-463. DOI: 10.1016/S0165-2370(00)00128-5
- Kandola, B. K., and Horrocks, A. R. (1996). "Flame-retardant treatments of cellulose and their influence on the mechanism of cellulose pyrolysis," *J. Macromol. Sci. Part C* 36(4), 721-794 (1996) DOI:10.1080/15321799608014859
- Kumar, S., Negi, Y. S., and Upadhyaya, J. S. (2010). "Studies on characterization of corn cob based nanoparticles," *Adv. Mat. Lett.* 1(3), 246-253. DOI: 10.5185/amlett.2010.9164
- Kumar, S., Choudhary V., and Kumar R. (2010). "Study on the compatibility of unbleached and bleached bamboo-fiber with LLDPE matrix," *J. Therm. Anal. Calorim.* 102, 751-761. DOI:10.1007/s10973-010-0799-4
- Li, H., Yang, Y. G., Wen, Y. F., and Liu, L. (2007). "A mechanism study on preparation of rayon based carbon fibers with (NH₄)₂SO₄/NH₄Cl/organosilicon composite catalyst system," *Compos. Sci. and Technol.* 67, 2675-2682. DOI: 10.1016/j.compscitech.2007.03.008
- Liu, Q. F., Lv, C. X., Yang, Y. G., He, F., and Ling, L. C. (2004). "Investigation on the effects of fire retardants on the thermal decomposition of wood-derived rayon fiber in

- an inert atmosphere by thermogravimetry–mass spectrometry,” *Thermochim. Acta.* 419, 205-209. DOI: 10.1016/j.tca.2003.12.014
- Mamleev, V., Bourbigot, S., Bras, M. L., and Yvon, J. (2009). “The facts and hypotheses relating to the phenomenological model of cellulose pyrolysis. Interdependence of the steps,” *J. Anal. Appl. Pyrolysis* 84(1), 1-17. DOI: 10.1016/j.jaap.2008.10.014
- Pappa, A., Mikedi, K., Tzamtzis, N., and Statheropoulos, M. (2006). “TG-MS analysis for study the effects of fire retardants on the pyrolysis of pine-needles and their components,” *Journal of Thermal Analysis and Calorimetry* 843, 655-661. DOI:10.1007/s10973-005-7201-y
- Piyali, D., Ganesh, A., and Wangikar, P. (2004). “Influence of pretreatment for deashing of sugarcane bagasse on pyrolysis products,” *Biomass Bioenergy.* 27(5), 445-457. DOI: 10.1016/j.biombioe.2004.04.002
- Proniewicz, L. M., Paluszkiwicz, C., Weselucha-Birczysimska, A., Majcherczyk, H., Bara simnski, A., and Konieczna, A. J. (2001). “FT-IR and FT Raman study of hydrothermally degraded cellulose,” *Mol. Struct.* 596(1), 163-169. DOI: 10.1016/S0022-2860(01)00706-2
- Richardson, S., and Gorton, L. (2003). “Characterisation of the substituent distribution in starch and cellulose derivatives,” *Anal. Chem. Acta.* 497(1), 27-65. DOI: 10.1016/j.aca.2003.08.005
- Schwanninger, M., Rodrigues, J. C., Pereira, H., and Hinterstoisser, B. (2004). “Effect of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose,” *Vib. Spectrosc.* 36(1), 23-40. DOI: 10.1016/j.vibspec.2004.02.003
- Sekiguchi, Y., and Shafizadeh, F. (1984). “The effect of inorganic additives on the formation, composition, and combustion of cellulosic char,” *J. Appl. Polym. Sci.* 29(4), 1267-1286. DOI: 10.1002/app.1984.070290421
- Statheropoulos, M., and Kyriakou, S. A. (2000). “Quantitative thermogravimetric mass spectrometric analysis for monitoring the effects of fire retardants on cellulose pyrolysis,” *Anal Chim Acta.* 409(1-2), 203-14. DOI: 10.1016/S0003-2670(99)00859-4
- Tang, Y. J., Yang, S. J., Zhang, N., and Zhang, J. H. (2014). “Preparation and characterization of nanocrystalline cellulose via low-intensity ultrasonic-assisted sulfuric acid hydrolysis,” *Cellulose* 21(1), 335-346. DOI: 10.1007/s10570-013-0158-2
- Teli, M. D., and Sheikh, J. (2013). “Modified bamboo rayon–copper nanoparticle composites as antibacterial textiles,” *Int. J. Biol. Macromol.* 61, 302-307. DOI: 10.1016/j.ijbiomac.2013.07.015
- Tiwari, S., and Bijwe, J. (2014). “Surface treatment of carbon fibers – A review,” *Procedia Technology.* 14, 505-512. DOI: 10.1016/j.protcy.2014.08.064
- Venkateswaran, R., Babu, S., Kumar, S. S., Pillai, M. A., and Sharma, P. V. (1990). “Thermal decomposition of viscose rayon in the presence of inorganic additives. A kinetic study,” *J. Appl. Polym. Sci.* 41(11-12), 2783-2811. DOI: 10.1002/app.1990.070411123
- Wang, X. L., Fang, G. Z., and Hu, C. P. (2007). “Influence of ultrasonic wave-activating treatment on structure and oxidation reactivity of microcrystalline cellulose,” *Chem. J. Chinese U.* 28(3), 565-567.

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