Effects of an inorganic ammonium salt treatment on the flame-retardant performance of lyocell fibers

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Lyocell fibers are produced by dissolving cellulose in a N-methylmorpholine-N-oxide/water solution. The resulting cellulose/N-methylmorpholine-N-oxide/water mixture is extruded through an orifice, drawn into an air gap, and then precipitated in a coagulation bath [1]. In contrast with rayon fibers, lyocell fibers have higher tenacity, a higher modulus, lower shrinkage when dried, and lower reductions of tenacity and the modulus when wet. Moreover, lyocell fibers are round and have molecular chains that are highly oriented along the fiber axis, and it is easy to control their fineness [2].

However, lyocell fibers are often subjected to high temperatures, which can cause degradation of the fibers. When lyocell fibers are heated, they undergo a series of interrelated physical and chemical changes, including physical changes in weight, strength, color, and crystallinity. In addition, heat treatment can cause the material to move through different transitional phases and expand or contract, melt and recrystallize or undergo major structural changes [3].

Thermal decomposition of the lyocell fibers leads to many kind of formations, such as solid residue, high-boiling point volatiles, and gaseous products. These kinds of products are formed through two competitive pathways. The first pathway involves many transformations, such as dehydration, rearrangement, carbonyl groups formation, the evolution of carbon monoxide and carbon dioxide, and the carbonaceous residue formation [4]. These phenomena take place rapidly in the presence of a variety of organic and inorganic catalysts, particularly Lewis acids, which catalyze the dehydration reactions. The second pathway competes with the first pathway and produces many oxygenated compounds and involves the thermal scission of glycosidic bonds between the glucopyranose units of cellulose [5]. These oxygenated compounds account for the majority of the weight loss of the solid residue. Therefore, it is important to control the reaction pathways during the initial pyrolysis stage to generate flame-retardant materials. Thus, flame-retardant enhanced lyocell fibers should be investigated for industrial applications. Recently, various treatment processes have been used to improve the flame-retardant properties of lyocell fibers. Because catalysts accelerate pyrolysis reactions, it is important to study the effects of catalysts on the pyrolysis of lyocell fibers. An effective catalyst should [6,7] decrease the pyrolysis temperature, increase the amounts of water and carbon dioxide produced during the reaction, and increase the amount of char formed.

Therefore, it is important to control the reaction pathways during the initial stage of pyrolysis when generating flame-retardant materials. In this study, the effects of two different inorganic ammonium salts, $(NH_4)_2SO_4$ and NH_4Cl, on the flame-retardant properties of lyocell fibers were studied. Combining these salts could have a synergistic effect on the pyrolysis of lyocell fibers, including the induction of a slow pathway that involves dehydration, rearrangement, the formation of carbonyl groups, the evolution of carbon monoxide and carbon dioxide, and the formation of a carbonaceous flame-retardant residue. The effects of this
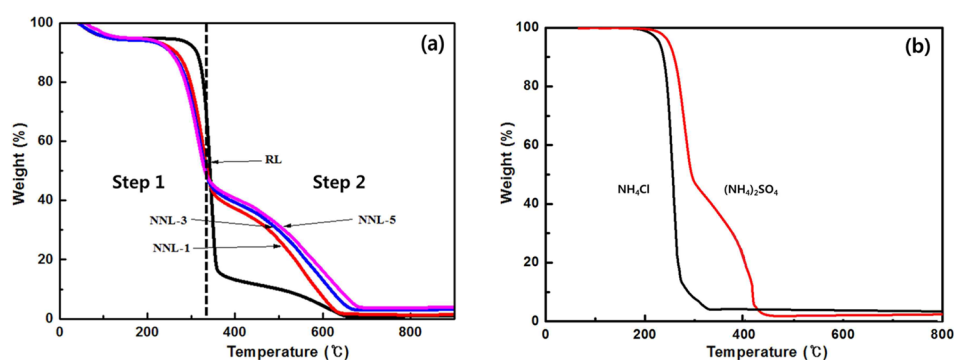
Fig. 1. (a) Thermal stability of lyocell fibers assessed by thermogravimetric analysis at a heating rate of 10 °C/min. (b) Thermal stability of $(NH_4)_2SO_4$ and NH_4Cl samples.

Table 1. IDT, T_{max} and E_a of the samples

Sample	Step I				Step II			
	RL	NNL-1	NNL-3	NNL-5	RL	NNL-1	NNL-3	NNL-5
IDT (°C)								
5°C/min	185	143	143	140	385	316	291	288
10°C/min	205	138	139	133	390	291	270	254
20°C/min	182	163	163	160	407	329	304	308
40°C/min	201	176	171	166	433	340	311	304
D.S.[a]	16	33	28	26	48	24	20	16
T_{max} (°C)								
5°C/min	289	228	225	224	452	415	393	408
10°C/min	301	208	205	202	466	420	380	369
20°C/min	314	243	243	238	479	439	426	423
40°C/min	328	256	252	249	503	445	420	430
D.S.[b]	39	28	27	25	51	30	27	22
E_a (kJ/mol)	144	157	161	172	183	273	284	361

IDT, initial degradation temperature; T_{max}, temperature at maximum weight loss rate; E_a, activation energy.
[a]D.S., degree of IDT shift (IDT at 40°C/min - IDT at 5°C/min).
[b]D.S., degree of T_{max} shift (T_{max} at 40°C/min - T_{max} at 5°C/min).

flame-retardant treatment method were investigated by studying the thermal decomposition of lyocell fibers.

In this study, lyocell fibers (Kolon, Gwacheon, Korea) with a length of 20 cm and an approximate weight of 10 g were used. For chemical treatment, the flame retardants, $(NH_4)_2SO_4$ and NH_4Cl, were of p.a. grade (>99.0%, Sigma-Aldrich, St. Louis, MO, USA), and were chosen because they were the most efficient reagents for yield enhancement [8]. For chemical treatment, $(NH_4)_2SO_4$ and NH_4Cl were used to induce yield enhancement after heat treatment. First, 10 g of raw lyocell fibers was immersed in 100 mL of a $(NH_4)_2SO_4/NH_4Cl$ solution [$(NH_4)_2SO_4$ concentrations: 1, 3, and 5 wt%; NH_4Cl concentrations: 2 wt%] fixed for 30 minutes at 60°C. Excess solution was removed by centrifugation and the remaining supernatant was dried over-

night at 70°C under a vacuum. The four samples were denoted as RL, NNL-1, NNL-3, and NNL-5 based on their respective $(NH_4)_2SO_4$ concentrations. A thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50H thermo analyzer (Shimadzu, Kyoto, Japan) at scan rates of 5, 10, 20, and 40°C/min under air and nitrogen (to investigate the integral procedure decomposition temperature [IPDT]) with flow rates of 2×10^{-5} m³/min. The char yield was obtained as the residual weight at 900°C in nitrogen. Limiting oxygen index (LOI, defined as the minimum fraction of O_2 in a gas mixture of O_2 and N_2 that will support flaming combustion) measurements were conducted using an apparatus (HC-2-type) in accordance with American Society for Testing and Materials (ASTM) D2863-77. The sample bars used for the test were 100 mm × 30 mm. The sample bars
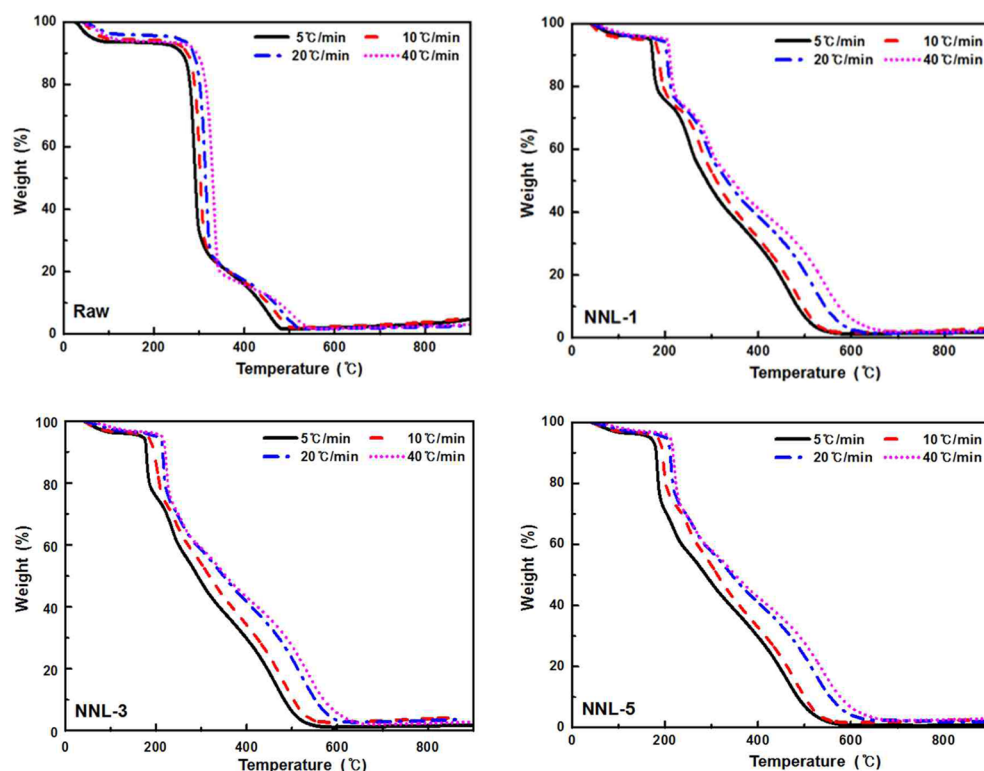
Fig. 2. Anti-oxidation properties of lyocell fibers assessed by thermogravimetric analysis.

were suspended vertically and ignited using a Bunsen burner. The flame was removed, and the timer was then started. The concentration of oxygen was increased when the flame on the specimen was either extinguished before burning for 3 min or 5 cm of the bar was burnt away. The oxygen content was adjusted until the limiting concentration was determined. To estimate the error and to determine the repeatability of the LOI test, the LOI value was measured five times for each sample.

The TGA curves in Fig. 1a show the effects of $(NH_4)_2SO_4$/ NH_4Cl treatment, which were obtained under nitrogen at a heating rate of 10°C, for thermal stabilization. It is known that $(NH_4)_2SO_4/NH_4Cl$ significantly lowers the decomposition temperature of cellulose. In Table 1, the T_{max} point of the $(NH_4)_2SO_4$/ NH_4Cl-treated lyocell fiber corresponded to the maximum weight loss point in the TGA curve.

All of the $(NH_4)_2SO_4/NH_4Cl$-treated lyocell fibers showed slight slope changes in the TGA curve observed, which appeared as two main shoulder peaks, denoted as step 1 and step 2. The step 1 shoulder peak at approximately 200°C was due to the thermal decomposition of $(NH_4)_2SO_4/NH_4Cl$ and the release of water and ammonia [9]. Moreover, the profile of the step 2 peak appears to reflect change of the combustion pathway, which was shifted to a higher temperature and became broader.

To examine the decomposition of samples, the TGA curves of $(NH_4)_2SO_4$ and NH_4Cl versus temperature were generated. As shown in Fig. 1b, $(NH_4)_2SO_4$ and NH_4Cl appeared to decompose in different temperature ranges. From the obtained data, NH_4Cl decomposed from approximately 200°C to 310°C, and $(NH_4)_2SO_4$ decomposed from 260°C to approximately 420°C.

Therefore, the combination of $(NH_4)_2SO_4$ and NH_4Cl provides continuous production of H_2SO_4 and HCl over a wider temperature range, likely from 200°C to 420°C, than the use of $(NH_4)_2SO_4$ or NH_4Cl alone. For this reason, we selected two inorganic ammonium salts for use in the catalyst system.

The char yields of the lyocell fibers modified with $(NH_4)_2SO_4$/ NH_4Cl tended to increase with increasing $(NH_4)_2SO_4$ content. The improved char yield was likely caused by the esterification of H_2SO_4 and primary hydroxyl groups in the fibers during the thermal decomposition of the $(NH_4)_2SO_4/NH_4Cl$-treated lyocell fibers. This interaction led to a thick and compact char [10]. This increasing char yield implied greater fire resistance of the sample, as it is posited that char formation would limit the production of combustion gases, inhibit combustion gases from diffusing to the pyrolysis zone, and protect the material surface from heat and air [11]. Therefore, the flame retardancy of lyocell fibers improved with the $(NH_4)_2SO_4/NH_4Cl$ treatment.

The anti-oxidation behavior was investigated by TGA, and the results are shown in Fig. 2. TGA investigations of each sample were performed at various heating rates to predict the anti-oxidation behavior during combustion and to calculate the activation energy. The TGA results evaluated at 5, 10, 20, and 40°C/min are depicted. In each case, the curve shifted to a higher temperature, as shown in Fig. 2. The degree of the shift decreased with the additives, indicating that the additives reduced the effects of the heating rate on the anti-oxidation properties of the sample. The initial degradation temperature (IDT, defined as the temperature onset) and the temperature at maximum weight loss rate (T_{max}, evaluated by differential thermal analysis) were
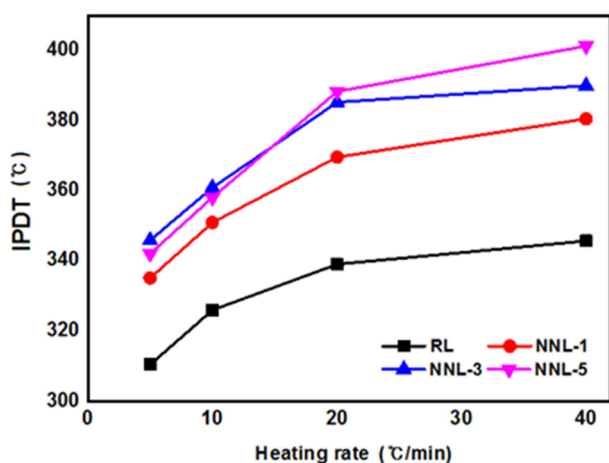
Fig. 3. Integral procedure decomposition temperature (IPDT) measured at various heating rates.

Fig. 4. Relationship between the limiting oxygen index (LOI) and char yield of the samples.

evaluated at 5, 10, 20, and 40°C/min and are presented in Table 1. All of the steps of the IDT decreased with the $(NH_4)_2SO_4/NH_4Cl$ additive but increased with the heating rate. This was attributed to the easy thermal decomposition by the dehydration of the lyocell fibers catalyzed by the phosphoric acid byproduct, which also contributed to quenching the pyrolysis system. At lower temperature, the decomposition reactions became slow, and thus a more stable char was produced. The degree of the shift decreased with the NH_4Cl concentration, indicating that $(NH_4)_2SO_4/NH_4Cl$ reduced the effects of the heating rate on the thermal properties of the sample.

The IPDT was calculated using the TGA data (measured under nitrogen flow) via the following equations [12,13]:

$$IPDT = A^* K^* (T_f - T_i) + T_i \qquad (1)$$

$$A^* = \left(\frac{S_1 + S_2}{S_1 + S_2 + S_3}\right) \qquad (2)$$

$$K^* = \left(\frac{S_1 + S_2}{S_1}\right) \qquad (3)$$

where T_i is the initial experimental temperature and T_f is the final experimental temperature. S_1, S_2, and S_3 are depicted by Doyle's proposition [12,13], and the calculated IPDTs are presented in Fig. 3. In all of the samples, the IPDT increased with higher heating rate, and the IPDT showed a higher value based on the effects of $(NH_4)_2SO_4/NH_4Cl$ treatment, indicating that the flame-retardant properties improved. This suggested that IPDT depended on surface degradation and that the formation of a protective film by the production of a charred layer provided the best result for high IPDTs based on the effects of $(NH_4)_2SO_4/NH_4Cl$ treatment. The IPDT increased by approximately 17% compared with the RL and NNL-5 samples.

The char yield and LOI are presented in Fig. 4. The char yield increased from 16.3% to 24.0% due to the effects of $(NH_4)_2SO_4/NH_4Cl$ treatment. It is well known that the char yield generated on a surface can act as a heat barrier and provide thermal insulation [14]. Therefore, it is expected that the increased char yield mitigated the lyocell fiber degradation. The LOI of the samples was investigated to determine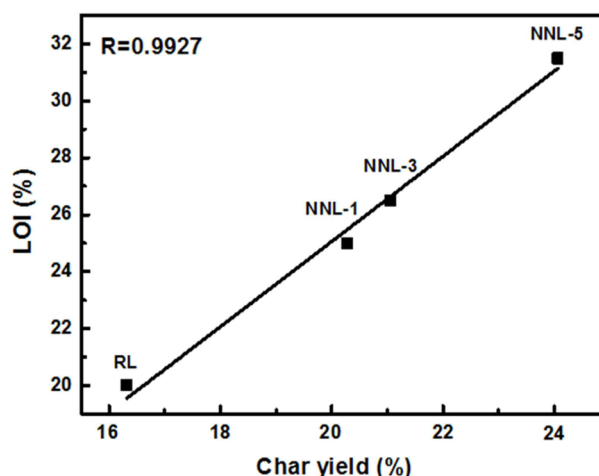 the essential oxygen content for ignition. The LOI increased from 21% to 31% due to the effects of the $(NH_4)_2SO_4/NH_4Cl$ treatment. The char of the samples formed during combustion and acted as a protective layer such that oxygen diffusion to the surface of the specimen was prevented, resulting in more oxygen necessary for the combustion process. These results were in good agreement with the findings for lyocell fibers modified with a $(NH_4)_2SO_4/NH_4Cl$ solution [9]. The relationship between the char yield and LOI could be observed by the regression line between them. The LOI increased, showing a first-order relationship with R = 0.9927. It appeared that the generated char yield, especially on the surface, resulted in a higher LOI, indicating that the generated char yield on the surface of the sample hindered the attack of oxygen radicals on the lyocell fibers.

The activation energy (E_a) was evaluated to investigate the anti-oxidation behavior of the fiber samples. E_a was calculated by the following equation derived from the Flynn, Wall, and Ozawa equations [14,15]:

$$E_d = -\frac{R}{C}\left[\frac{\Delta \log \Phi}{\Delta(1/T_r)}\right] \qquad (4)$$

where T_r is the weight loss temperature and Φ is the heating rate (°C/min). C is a constant (0.4521). The calculated E_a is presented in Table 1. All of the steps of the activation energy increased with increasing amounts of $(NH_4)_2SO_4/NH_4Cl$ treatment. In step 1, the activation energy of the NNL-5 sample was approximately 20% higher than that of the untreated sample (144 compared with 172 kJ/mol). This result was ascribed to the formation of thermally stable structures during the initial stages of the thermo-oxidative reactions in step 1. The results also show that in the step 2 atmosphere, the activation energy of the NNL-5 sample was approximately 97% higher than that of the untreated sample. The decomposition of the $(NH_4)_2SO_4/NH_4Cl$-treated sample proceeded at a slightly higher rate, presumably due to a change in the decomposition pathway of the lyocell fibers.

Lyocell fibers were treated with a $(NH_4)_2SO_4/NH_4Cl$ solution as a catalyst for flame-retardant behavior. The effects of the $(NH_4)_2SO_4/NH_4Cl$ solution on the thermal degradation and

flammability of lyocell fibers were investigated. The flame-retardant properties of the lyocell fibers tended to increase with increasing NH_4Cl content. The lyocell fiber modified with NH_4Cl up to 5 wt%, sample NNL-5, provided the best linear burning rate. The LOI and char yield were also studied to investigate the behavior during combustion and the mechanism of action of the $(NH_4)_2SO_4/NH_4Cl$ treatments. $(NH_4)_2SO_4/NH_4Cl$ treatment increased the char yield, which also increased the LOI and lowered the rate of degradation of the lyocell fibers, which led to a thick and compact char. The IPDT significantly increased, and the activation energy increased by a factor, indicating that the flame-retardant properties of the $(NH_4)_2SO_4/NH_4Cl$-treated lyocell fibers improved.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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