Improved flame retardant performance of cellulose fibers following fluorine gas treatment

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Abstract
To improve the flame retardant performance of cellulose fibers, fluorine functional groups were introduced under various controlled fluorination conditions. The properties of the fluorinated cellulose fibers were analyzed by X-ray photoelectron spectroscopy and a thermogravimetric analysis. The fluorine functional group content in the fluorinated cellulose fibers increased with an increase in the fluorination temperature. However, the fluorination reaction increased the char yield and decreased the rate of degradation of the cellulose fibers by introducing donors, enabling the formation of a thick and compact char layer. Therefore, the flame retardant properties of cellulose fibers were improved following the fluorination treatment.

Keywords: fluorination; flame retardant; cellulose fiber; thermal degradation; integral procedure decomposition temperature

1. Introduction

The precursor of the cellulose fibers used to prepare carbon fibers has very a low carbon content (44.4%), and after carbonization, the yield does not exceed 10 to 15\% [1-3]. To produce cellulose-based carbon fibers, the carbonization yield of the cellulose precursor should be increased as much as possible.

The pyrolysis of cellulose fibers typically leads to the formation of a solid residue (char), high-boiling-point volatiles (tar), and gaseous products. These products are formed by two competitive pathways. The first pathway involves dehydration, rearrangement, and the formation of carbonyl groups, carbon monoxide, carbon dioxide, and a carbonaceous residue. These reactions are accelerated in the presence of a variety of organic and inorganic catalysts, particularly Lewis acids, which catalyze the dehydration reactions [4,5].

In the second pathway, which competes with the first, the thermal scission of the glycosidic bonds between glucopyranose units of cellulose produces many oxygenated compounds. These oxygenated compounds account for the dramatic weight loss of the solid residue. Therefore, control of the reaction pathways in the initial stage of pyrolysis is important for the development of flame retardant materials. In this light, cellulose fibers with enhanced flame retardant properties should be investigated for industrial application. Recently, various treatment processes have been used to improve the flame retardant properties of cellulose fibers [6,7].

Since catalysts accelerate the pyrolysis reactions, studies on the effects of catalysts on the pyrolysis of cellulose fibers are essential. An effective catalyst should have the following functions. First, the catalyst should decrease the pyrolysis temperature to a lower range. Second, it should increase the amounts of water and carbon dioxide produced in the reaction. Finally, it should increase the amount of char formed [8-10].

Therefore, control of the reaction pathways during the initial stage of pyrolysis is an important requirement of the flame retardant treatment. In this study, to increase the thermal
degradation properties of cellulose fibers, fluorine functional groups were introduced. Fluorine functional groups in particular can increase the thermal degradation properties of cellulose more than other functional groups. Fluorination is one of the methods for modifying a surface with fluorine functional groups [11-13]. The fluorination treatment enhanced the 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 residue and thereby improve the flame retardancy of cellulose fibers. In addition, the surface and thermal degradation properties of the fluorinated cellulose fibers were evaluated, and the carbonization yield was investigated as a function of the fluorination conditions.

2. Experimental

2.1. Fluorination of cellulose

The cellulose fibers (lyocell, α-cellulose, 1650 denier) used in this study were obtained from Kolon Industries (Korea, α-cellulose, fiber diameter: ~12 μm). The cellulose fibers were cleaned by immersion in acetone at room temperature for 1 h, washing with distilled water, and then drying at 100°C for 1 h. The cellulose fibers were subjected to fluorination by fluorine gas (98%) in a batch reactor made of nickel with an outer electric furnace. The cellulose fibers were loaded onto a nickel boat in the reactor and degassed under a vacuum at 60°C for 1 h. After degassing, the fluorination reaction was carried out at temperatures from room temperature to 180°C for 10 min at 1 bar. The prepared samples were labeled according to the fluorination conditions as R-Ce (raw cellulose fibers), F-Ce-RT (cellulose fibers fluorinated at room temperature), F-Ce-60 (cellulose fibers fluorinated at 60°C), F-Ce-120 (cellulose fibers fluorinated at 120°C), and F-Ce-180 (cellulose fibers fluorinated at 180°C).

2.2. Characterization of fluorinated cellulose

The surface properties of the samples were investigated using X-ray photoelectron spectroscopy (XPS; ThermoVG Scientific, UK). The thermal degradation properties of the samples were investigated via a thermogravimetric analysis (TGA; Mettler-Toledo Inc., USA). TGA scans were recorded at 10°/min from 30 to 1000°C under a constant flow of nitrogen. Additionally, the integral procedure decomposition temperature (IPDT) was calculated from the TGA data. The fluorinated cellulose fibers were carbonized in a nitrogen atmosphere at 800°C for 1 h at a heating rate of 5°C/min, and their carbonization yield was obtained by measuring the residual weight after carbonization.

3. Results and Discussion

3.1. Surface properties of the cellulose fibers after fluorination

The surface chemical bonds on the fluorinated cellulose fibers were analyzed by XPS; their XPS survey spectra and elemental contents are shown in Fig. 1. Three main peaks were identified; these peaks are marked as F1s, O1s, and C1s. The intensity of the F1s peak increased with increasing fluorination temperature, whereas the intensities of the C1s and O1s peaks decreased. However, in the case of fluorination at 180°C (F-Ce-180), the intensities of the C1s and F1s peaks decreased, whereas that of the O1s peak increased. Im et al. [14] reported the removal of the introduced fluorine functional groups from the surface by the application of high heat energy during thermal fluorination. Therefore, we hypothesize that the F1s peak of F-Ce-180 decreased due to removal of fluorine functional groups by the high heat energy applied during thermal fluorination.

The chemical compositions of the samples are shown in Fig. 2 and Table 1. In the case of R-Ce (Fig. 2a), three main peaks were observed at 285, 286.6 and 288.3 eV, which correspond to C-C, C-O, and O-C-O bonds, respectively. In the case of the fluorinated cellulose fibers, new components, such as C-C, C=O, CF, CF2, and CF3 bonds, appeared [15-17]. The fluorination process used fluorine radicals produced from the decomposition of fluorine gas. The fluorine radicals converted C-C bonds to C=O bonds, and the created C=O bonds act as precursors for char formation through either aromatization or crosslinking [18,19]. The number of fluorine functional groups introduced on the cellulose fibers increased with increasing fluorination temperature; correspondingly, the number of CF1 bonds (perfluorinated carbon) in the cellulose also increased. The number of C-O and O-C-O bonds decreased, and the number of double bonds (C=O, C=C bonds) increased with increasing fluorination temperature. However, at a reaction temperature of 180°C (F-Ce-180), no CF3 bonds were observed because of the removal of the introduced fluorine, and F-Ce-180 exhibited the highest C-C bond content.

3.2. The thermal degradation properties of cellulose fibers after fluorination

The thermal degradation behavior of the fluorinated cellulose fibers was investigated by TGA and the results are shown in Fig. 3. All the fluorinated cellulose fibers show slight differences in the slope of the TG curve, which appears as two shoulder peaks. The first step corresponding to the shoulder peak at approximately 200°C is due to the fast-thermal decomposition of

![Fig. 1. XPS survey spectra of (a) R-Ce, (b) F-Ce-RT, (c) F-Ce-60, (d) F-Ce-120, and (e) F-Ce-180.](http://carbonlett.org)
greater fire resistance of the sample, as it has been proposed that char formation limits the production of combustion gases, inhibits the diffusion of combustion gases into the pyrolysis zone, and protects the material surface from heat and air [22]. Therefore, the flame retardant properties of the cellulose fibers improved with the fluorination treatment.

The initial degradation temperatures (IDTs) of F-Ce-RT, F-Ce-60, and F-Ce-120 were lower than that of R-Ce. In general, short-chain cellulose has a low IDT. The XPS results reveal that the C-O-C bonds of the cellulose fibers, which are con-

<table>
<thead>
<tr>
<th>Component</th>
<th>Peak position (eV)</th>
<th>R-Ce</th>
<th>F-Ce-RT</th>
<th>F-Ce-60</th>
<th>F-Ce-120</th>
<th>F-Ce-180</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>C=C</td>
<td>284.1</td>
<td>-</td>
<td>1.2</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>C2</td>
<td>C-C</td>
<td>285.0</td>
<td>75.8</td>
<td>15.0</td>
<td>14.3</td>
<td>13.7</td>
</tr>
<tr>
<td>C3</td>
<td>C=O</td>
<td>286.6</td>
<td>14.3</td>
<td>8.3</td>
<td>8.0</td>
<td>4.2</td>
</tr>
<tr>
<td>C4</td>
<td>C=O</td>
<td>287.6</td>
<td>-</td>
<td>1.2</td>
<td>2.4</td>
<td>3.1</td>
</tr>
<tr>
<td>C5</td>
<td>O-C-O</td>
<td>288.3</td>
<td>9.9</td>
<td>6.6</td>
<td>5.9</td>
<td>4.3</td>
</tr>
<tr>
<td>C6</td>
<td>C-F (semi-covalent)</td>
<td>288.4</td>
<td>-</td>
<td>3.8</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>C7</td>
<td>C-F (covalent)</td>
<td>289.3</td>
<td>-</td>
<td>5.0</td>
<td>6.1</td>
<td>1.1</td>
</tr>
<tr>
<td>C8</td>
<td>CF₂</td>
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<td>-</td>
<td>28.4</td>
<td>25.8</td>
<td>20.9</td>
</tr>
<tr>
<td>C9</td>
<td>CF₂-CF₂</td>
<td>292.4</td>
<td>-</td>
<td>16.4</td>
<td>15.9</td>
<td>14.9</td>
</tr>
<tr>
<td>C10</td>
<td>CF₂-CF₃</td>
<td>293.3</td>
<td>-</td>
<td>8.2</td>
<td>11.2</td>
<td>18.5</td>
</tr>
<tr>
<td>C11</td>
<td>CF₃</td>
<td>294.3</td>
<td>-</td>
<td>5.9</td>
<td>8.2</td>
<td>17.5</td>
</tr>
</tbody>
</table>
is the precursor of char formation by either aromatization or crosslinking) content than F-Ce-RT following fluorination. Accordingly, the IPDT of F-Ce-180 was higher than that of F-Ce-RT because of its higher C=C bond content.

3.3. The carbonization yield of the cellulose fibers after fluorination

The carbonization yields of the fluorinated cellulose fibers were obtained by measuring the residual weight after carbonization in a nitrogen atmosphere at 800°C for 1 h with a heating rate of 5°C/min, and the results are shown in Fig. 5. The trend in the carbonization yield of the fluorinated cellulose fibers was similar to the trends of the IPDT and the char yields. The carbonization yields of the fluorinated cellulose fibers increased from 16.0 to 24.4% after fluorination at 120°C (an increase of 52.5% compared to the carbonization yield achieved with pure cellulose fibers).

To demonstrate the effect of the fluorination of cellulose on the carbonization process, R-Ce and F-Ce-120 were thermally treated in a nitrogen atmosphere at 350°C for 1 min. The surface chemical bonds on the thermally treated R-Ce and F-Ce-120 samples were analyzed by XPS; the resulting XPS survey spectra and elemental contents are shown in Fig. 6. The C 1s and O 1s peaks of the thermally treated R-Ce...
4. Conclusions

To improve the carbonization yield, the thermal degradation of cellulose fibers was controlled by the introduction of fluorine functional groups. Fluorination (which is a method of introducing fluorine functional groups) was carried out at various temperatures from room temperature to 180°C for 10 min at 1 bar. The fluorine concentration increased with increasing fluorination temperature, whereas the carbon and oxygen concentrations decreased. However, at a high fluorination temperature (at 180°C), the fluorine concentration decreased because of the high heat energy. Therefore, the fluorination reaction increased the char yield and decreased the rate of cellulose fiber degradation by introducing donors, enabling the formation of a thick and compact char layer. The IPDT increased as a function of the fluorine and oxygen contents, indicating that the flame retardant properties of the cellulose fibers were improved by the fluorination treatment. Based on these findings, the introduction of fluorine functional groups increased the carbonization yield of cellulose fibers by increasing the number of C=C bonds through thermal degradation of the fluorine functional groups during the carbonization process. Fluorination at 120°C increased the carbonization yield by 52.5% compared to that achieved with pure cellulose fibers.

Conflict of Interest

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

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