Microstructural changes of polyacrylonitrile-based carbon fibers (T300 and T700) due to isothermal oxidation (1): focusing on morphological changes using scanning electron microscopy

Seong-Moon Oh, Sang-Min Lee, Dong-Su Kang and Jae-Seung Roh*

School of Materials Science and Engineering, Kumoh National Institute of Technology, Gumi 39177, Korea

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*Corresponding Author
E-mail: jsroh@kumoh.ac.kr
Tel: +82-54-478-7744

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Abstract
Polyacrylonitrile (PAN)-based carbon fibers have high specific strength, elastic modulus, thermal resistance, and thermal conductivity. Due to these properties, they have been increasingly widely used in various spheres including leisure, aviation, aerospace, military, and energy applications. However, if exposed to air at high temperatures, they are oxidized, thus weakening the properties of carbon fibers and carbon composite materials. As such, it is important to understand the oxidation reactions of carbon fibers, which are often used as a reinforcement for composite materials. PAN-based carbon fibers T300 and T700 were isothermally oxidized in air, and microstructural changes caused by oxidation reactions were examined. The results showed a decrease in the rate of oxidation with increasing burn-off for both T300 and T700 fibers. The rate of oxidation of T300 fibers was two times faster than that of T700 fibers. The diameter of T700 fibers decreased linearly with increasing burn-off. The diameter of T300 also decreased with increasing burn-off but at slower rates over time. Cross-sectional observations after oxidation reactions revealed hollow cores in the longitudinal direction for both T300 and T700 fibers. The formation of hollow cores after oxidation can be traced to differences in the fabrication process such as the starting material and final heat treatment temperature.

Keywords: polyacrylonitrile-based carbon fiber, isothermal oxidation, burn-off, microstructure, morphology

1. Introduction

Polyacrylonitrile (PAN)-based carbon fibers, which use PAN as a precursor, are fabricated into lightweight, high-strength carbon fibers through spinning, stabilization, and carbonization [1,2]. They are known for their high specific strength, melting point, elastic modulus, thermal resistance, and thermal conductivity [3-5]. Recently, PAN-based carbon fibers have seen wide use in leisure, aviation, aerospace, military, and energy sectors because they satisfy industrial demands for lightweight and high-strength materials [6,7].

However, carbon fibers and other carbon materials break down into CO or CO$_2$ when oxidized in air at temperatures higher than 500°C [8]. Since oxidation reactions at high temperatures weaken the properties of carbon fiber composite materials, various studies have been conducted to resolve this issue [9,10]. This highlights the importance of understanding the oxidation reactions of carbon fibers, which are used as a reinforcement for composite materials.

Most research on the oxidation reactions of carbon fibers has focused on the production of activated carbon fibers or the oxidation mechanism of pitch-based carbon fibers. On the other hand, there have been few studies on the oxidation reaction of PNA-based
Microstructural changes of PAN CFs (T300 and T700) due to isothermal oxidation

In this study, PAN-based carbon fibers, most commonly used as a reinforcement for C-C composite materials or carbon fiber reinforced plastics (CFRP), were isothermally oxidized in air. The microstructural changes resulting from oxidation reactions were examined. Among the various microstructural changes, this study focused on morphological changes using scanning electron microscope (SEM).

2. Experimental

2.1. Raw materials and sample preparations

The raw carbon fibers used in this study were PAN-based carbon fibers T300 (3k) and T700 (12k) fabricated by Toray Advanced Materials (Seoul, Korea). The surface of the raw materials and desized carbon fibers was observed using a SEM (JSM-6500F, JEOL, Japan), and the results are shown in Fig. 1. As shown in Fig. 1a, the texture on the surface of T300 fibers was well-developed. The T700 fibers shown in Fig. 1b had a smoother surface with less texture. Fig. 1c and d present observations of the desized fibers after exposing them to air at 400°C for 1 h. The desized T300 fibers had more distinct texture lines than the raw fibers. The desized T700 fibers showed some texture, but this was not as developed as the texture of the T300 fibers. Isothermal oxidation reactions in this study were carried out using the desized carbon fibers.

2.2. Isothermal oxidation

The desized carbon fibers were isothermally oxidized using a thermogravimetric analyzer (TGA) (Auto TGA Q502, TA Instruments, USA). The fibers used in the TGA analysis were cut to 5.0 mm with an initial weight of 4.5 ± 0.1 mg. The gas for oxidation was air, with a flow rate of 50 mL/min. The isothermal oxidation reactions were carried out at 700°C, and a graph of the results is shown in Fig. 2. As can be seen from the isothermal oxidation graph, oxidation reactions were faster for T300 than T700 at 700°C. T300 fibers completed oxidation in 46.24 min, and T700 fibers did so in 82.25 min.

2.3. Microstructure

Microstructural changes of PAN CFs (T300 and T700) due to isothermal oxidation were observed using SEM after isothermal oxidation. Oxidation samples were obtained by adjusting the oxidation time based on the graph of Fig. 2. The amount of oxidation of the samples in relation to the oxidation time is represented as burn-off (%), and the conditions are presented in Table 1. SEM was employed to observe the surface and cross-section to evaluate morphological changes.

3. Results and Discussion

3.1. Oxidation rate

For a quantitative comparison of oxidation rates between the two fibers, the oxidation rate was calculated from the isothermal oxidation graph. As shown in (1), the oxidation rate was expressed as the change in weight with burn-off.

\[
\text{mg}_{\text{lost}} / (\text{mg} \times \text{min})
\]
bers showed a decrease in the rate of oxidation with increasing burn-off. The normalized rate of T300 fibers at 20% burn-off was 29.00, and this decreased by 14.87 times to 1.95 at 80% burn-off. The normalizing rate of T700 fibers at 20% burn-off was 14.59 times faster than the rate at 80% burn-off.

The oxidation rate tends to decrease with increasing burn-off because the reduced weight results in a fewer number of carbon atoms of the fiber contributing to reactions with O\textsubscript{2} in air. Another possibility is that there is sufficient O\textsubscript{2} adsorbed on the surface of carbon fibers, but the emission of CO from the surface over time interferes with the adsorption of the reacting gas.

At all burn-off amounts, the rate of oxidation of T300 fibers was two times faster than that of T700 fibers. This indicates that T700 fibers have a greater resistance to oxidation than T300 fibers.

### 3.2. Surface morphology

Fig. 4 presents ×1000 magnification of the surface of T300 and T700 fibers using SEM. As shown in the im-

![Fig. 3. Plots for oxidation rate and normalized rate as a function of burn-off.](image)

### Table 2. Oxidation rate and normalized rate as a function of burn-off

<table>
<thead>
<tr>
<th>Burn-off (%)</th>
<th>Oxidation rate (mg\textsubscript{m}/[mg \times min])</th>
<th>Normalized rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T300</td>
<td>T700</td>
</tr>
<tr>
<td>20</td>
<td>0.1073</td>
<td>0.0540</td>
</tr>
<tr>
<td>50</td>
<td>0.0291</td>
<td>0.0148</td>
</tr>
<tr>
<td>80</td>
<td>0.0072</td>
<td>0.0037</td>
</tr>
</tbody>
</table>

where mg\textsubscript{m} is measured weight, mg\textsubscript{i} is initial weight, and min is oxidation time. Table 2 shows the oxidation rates for varying burn-off values of 20%, 50%, and 80% in the isothermal oxidation graph of Fig. 2. This relationship is presented as a graph in Fig. 3a. The normalized rates in Table 2 are the standardized values of other samples when the rate of T700 fibers at 80% burn-off is set as 1.0. The relationship between oxidation rate and burn-off is given in Fig. 3b.

As shown in Fig. 3 and Table 2, both the T300 and T700 fi-

![Fig. 4. Scanning electron microscope images (×1k); (a) desized T300 fiber, (b) 27.10% oxidized T300 fiber, (c) 45.16% oxidized T300 fiber, (d) 65.96% oxidized T300 fiber, (e) desized T700 fiber, (f) 28.06% oxidized T700 fiber, (g) 51.56% oxidized T700 fiber, (h) 71.66% oxidized T700 fiber.](image)
3.3. Cross-sectional morphology

Fig. 7 shows the cross-section of carbon fibers before and after isothermal oxidation. The cross-sectional observations revealed hollow cores in the longitudinal direction after isothermal oxidation, similar to the shape of hollow fibers [19,20]. According to the model proposed by Barnet and Norr [21], the crystallinity weakens towards the center of PAN-based carbon fibers. Thus, the formation of hollow cores, as shown in Fig. 7, can be explained by the difference in oxidation rates, arising from the difference in crystallinity between the surface and the center. This results from differences in the fabrication process such as the starting material and the final heat treatment temperature.

This study employed SEM to observe morphological changes of T300 and T700 carbon fibers after isothermal oxidation. The difference in oxidation behavior between the two fibers is due to the difference in crystallinity between the surface and the center. As future work, Ramam spectroscopy and X-ray diffraction spectroscopy will be
of hollow cores after oxidation is due to the difference in crystallinity between the surface and the center, which can be traced to differences in the fabrication process such as the starting material and the final heat treatment temperature.

Conflict of Interest

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

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References


