

X-ray diffraction analysis of the crystallinity of phenolic resin-derived carbon as a function of the heating rate during the carbonization process

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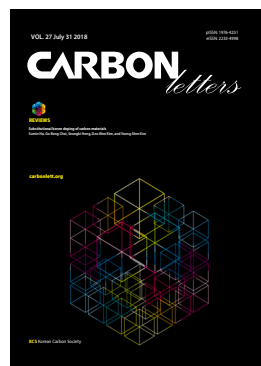
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The properties of bulk graphite and carbon-carbon (C/C) composite products, including their mechanical and electrical properties and thermal conductivity, may be determined by not only the size, content, shape, and dispersion of the filler materials but also by the crystallographic structure of the binding materials [1,2]. As the substituent hydrogen is removed during the carbonization process, an organic binder is converted into a carbonaceous material, specifically an aromatic carbon molecule in which large polycyclic aromatics are stacked. Reports have shown that a thermal treatment of carbon materials at a temperature exceeding 2500°C converts the crystal structure into a graphite structure or a graphite-like structure, indicating that the crystallinity of the resulting structure is higher at a higher thermal treatment temperature [3,4].

Improved crystallinity for phenol resin with an increase in the heat treatment temperature has been demonstrated in various studies [3]. However, research on the heating rate is lacking. This study aimed to investigate the change in the crystallinity through an X-ray diffraction analysis according to heating rate variations during the carbonization process of phenol resin. In the manufacturing of bulk graphite and a C/C composite, an inappropriate heating rate at the carbonization step can deform and damage specimens. Hence, the heating rate is kept as low as possible in the carbon industry to minimize defects. Experimental results on the heating rate are essential for the manufacturing of specimens, but few studies have been conducted on the crystallographic structure of organic precursors used as a binder considering the heating rate.

This study is expected to serve as base data for product quality control in the manufacturing of bulk graphite and C/C composites using phenol resin as a binder material. The precursor used in the present study was a novolac-type phenol resin powder (Kangnam Chemical Co. Ltd., Korea) which is presently used and considered to be an important binder material for bulk graphite and C/C composites.

The phenol resin powder (0.5±0.02 g) was put into a silicone mold (13.0×13.0 mm) and cured at 150°C for 6 h. The cured phenol resin was then heated to 1000°C (N₂, 2l/min) at heating rates of 1, 5, 10, 15, and 20°C/min, after which it was kept at 1000°C for 10 min to prepare phenolic-resin-derived carbon. The total heating times from room temperature to 1000°C, according to the heating rate, were 1000 (1°C/min), 200 (5°C/min), 100 (10°C/min), 66.7 (15°C/min), and 50 min (°C/min).

Samples for the X-ray diffraction (XRD; D-MAX/2500-PC, Rigaku, Japan) analysis were prepared by milling phenolic-resin-derived carbon with a diameter of 63 μm or smaller via a screening classification process. The wavelength of the X-ray target (Cu-Kα₁) used for the XRD was 1.5406 Å, and the acceleration voltage and applied current were 40 kV and 200 mA, respectively. The XRD peaks were obtained in a scanning range of 5 to 60° and at a scanning rate of 1°/min by 2θ continuous scanning.

Fig. 1 shows the XRD spectra of the phenolic-resin-derived carbon powder as a function of the heating rate. A broad (002) peak was found at around 25° with a large background area under the peak. A 10l peak that was not decomposed into (100) and (101) peaks was found between 40 and 45°. As the heating rate was increased, the 2θ position on the (002) plane shifted slightly to a lower angle. The XRD results showed that the phenolic-resin-derived

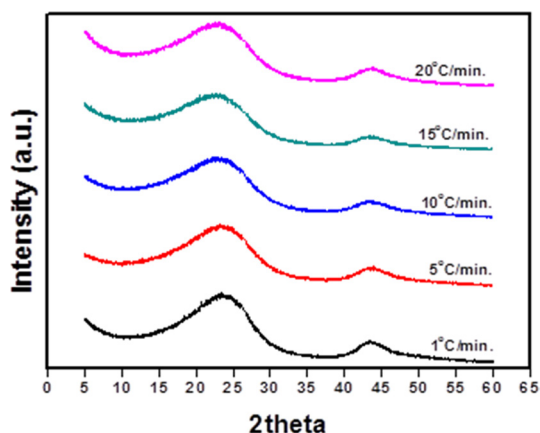


Fig. 1. X-ray diffraction spectra of the phenolic resin-derived carbon powder as a function of the heating rate.

carbon powder is a hard carbon material with a high amorphous carbon content.

A few researchers have reported a mixed structure of crystalline carbon and amorphous carbon examined by means of an XRD analysis [5-7]. The Lc and La values of various carbon-based materials were reported on the nanometer scale. This suggests that the internal structure of carbonized materials is composed of such a mixture, characterized by random mixing and interconnections of crystalline carbon nano-clusters and amorphous carbon nano-clusters. Franklin [5] and Ergun and Tiensuu [6] proposed that amorphous carbon does not contribute to the peak strength in X-ray diffractograms and that it appears in the background. Based on findings by Franklin, Lu et al. [8] expressed the (002) peak strength as the sum of crystalline and amorphous carbon according to an X-ray analysis of coal. A quantitative analysis was also carried out.

The ratio of the diffraction intensity of crystalline carbon nano-clusters ($I_{\text{crystalline}}$) to the diffraction intensity of amorphous carbon nano-clusters ($I_{\text{amorphous}}$), $I_{\text{crystalline}}/I_{\text{amorphous}}$, is proportional to the weight ratio of the individual carbon nano-clusters if the chemical compositions of the crystalline carbon nano-clusters and the amorphous carbon nano-clusters are identical [9]. The relative fractions of the crystalline carbon nano-clusters and the amorphous carbon nano-clusters were calculated using the maximum intensity of the (002) peak by the method shown in Fig. 2a. The fractions of the crystalline carbon nano-clusters and the amorphous carbon nano-clusters were calculated using the following equations:

$$\text{Crystalline fraction (\%)} = (I_{\text{crystalline}} / I_{\text{total}}) \times 100$$

$$\text{Amorphous fraction (\%)} = (I_{\text{amorphous}} / I_{\text{total}}) \times 100$$

Fig. 2b shows the calculated fractions of the crystalline carbon nano-clusters and the amorphous carbon nano-clusters. The crystalline fraction decreased as the heating rate was increased. The crystalline fractions were 73.0 and 72.9% at 1 and 5°C/min, respectively. The crystalline fraction was found to have decreased to 67.6, 66.5, and 67.0, at 10, 15, and 20°C/min, respec-

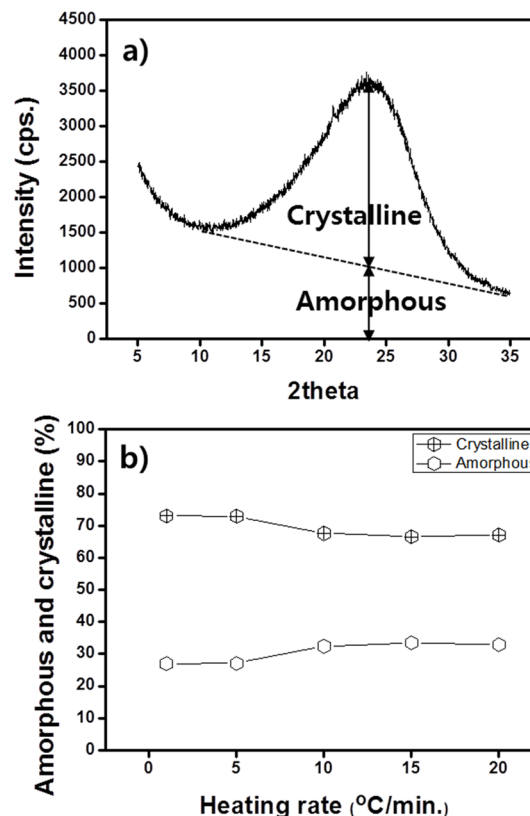


Fig. 2. Calculated method and results of crystalline and amorphous carbon nano-clusters: (a) calculated outcome when using the maximum intensity of the 002 peak, and (b) calculated fractions of the crystalline carbon nano-cluster and the amorphous carbon nano-cluster.

tively. The crystalline fraction at 20°C/min was lower than that of 1°C/min by 6.0%. XRD theory has shown that asymmetric XRD peaks can be found when a sample has a stacked crystal structure or when the sample composition is not uniform [10]. A carbon material having a graphite structure shows asymmetry of the (002) peak due to stacking defects.

Research that attempted a quantitative analysis of the structural parameters (d_{002} , Lc) of an asymmetric (002) peak in an X-ray diffractogram was reported in a study by Franklin [7], who found that two or three graphitization phases exist for non-graphitizing types of carbons. Afterwards, many researchers reported structural parameter analysis results after decomposing the asymmetric (002) peak observed in coal and hard carbon materials into two to three peaks. Among them, Honda et al. [11] and Kobayasi et al. [12] decomposed the (002) peak from an XRD analysis of graphitized phenol in the temperature range of 2400 to 3000°C into three domains with sharp peaks of 26 and 26.5° and with a broad peak of 26°; they then calculated the d_{002} and Lc values for each peak.

Lu et al. [8] and Manoj and Kunjomana [13] presented a decomposition method for the (002) peak in an XRD analysis of coal. The asymmetric (002) peak was decomposed into a γ -band of approximately 20° and an H-band of about 26°, and each band was defined by the aromatic and aliphatic carbon atom numbers. After decomposing the (002) peak, the plane spacing and Lc were calculated using the 2 θ and FWHM of the H-band

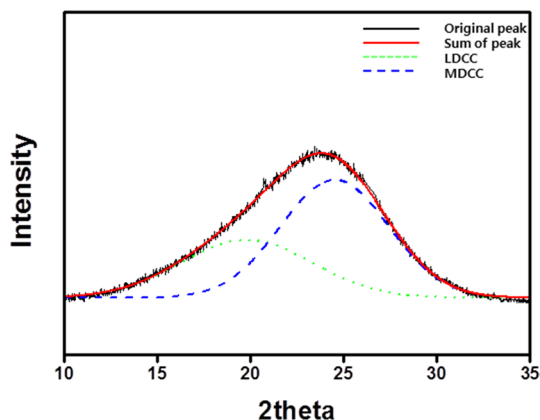


Fig. 3. Curve-fitting of two Gaussian peaks for the carbonized phenolic resin in the XRD spectrum with a 2θ range of 10° – 35° .

of approximately 26° .

In this study, the (002) peak of phenolic-resin-derived carbon could be decomposed into two bands, which were defined as less developed crystalline carbon (LDCC) and more developed crystalline carbon (MDCC). The decomposed peaks were quantitatively analyzed by the following method.

With regard to the (002) peak, the base point found between 10° and 15° was connected to 35° with a straight line to remove the background. Then, after smoothing, the band was decomposed into two bands by Gaussian fitting. All of the correlation coefficients of the band deconvolution exceeded 0.99. Fig. 3 shows the (002) peak deconvolution method. Each of the interlayer spacings and crystal sizes were obtained from each band. L_c and L_a values were calculated using the Scherrer equation [15]. The interlayer spacing, L_c , and the L_a values of LDCC and MDCC were slightly dependent on the heating rate, but neither showed a distinctive trend. This indicates, as is widely known already, that the main factor affecting the structural parameters of carbon materials is the thermal treatment temperature [15].

Although the structural factors (i.e., d_{hkl} , L_c , and L_a) were not significantly affected by the heating rate during the carbonization step, the crystal quality (i.e., the relative amounts of LDCC and MDCC) could change depending on the heating rate. The relative area-based fractions of LDCC and MDCC were calculated using the following equation:

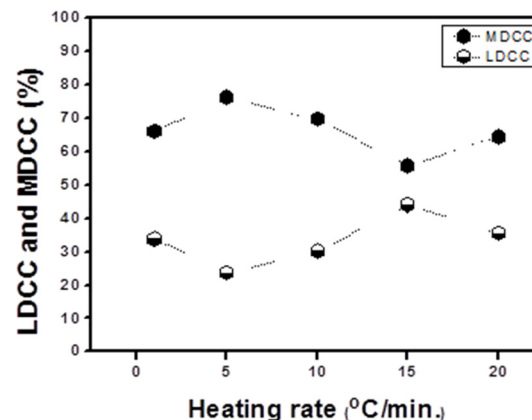


Fig. 4. Fractions of LDCC and MDCC as a function of the heating rate.

$$\text{LDCC fraction (\%)} = (\text{Area}_{\text{LDCC}} / \text{Area}_{\text{total}}) \times 100$$

$$\text{MDCC fraction (\%)} = (\text{Area}_{\text{MDCC}} / \text{Area}_{\text{total}}) \times 100$$

Table 1 summarizes the interlayer spacing, L_c , and the L_a value of the phenolic resin-derived carbon.

Fig. 4 shows the calculated relative LDCC and MDCC fractions as a function of the heating rate. These results showed that the heating rate for carbonization affects the MDCC and LDCC fractions. The MDCC fraction was highest (76.3%) at a heating rate of $5^\circ\text{C}/\text{min}$ and lowest (55.8%) at $15^\circ\text{C}/\text{min}$.

Subsequently, the decrease in the crystallinity with an increase in the heating rate during the carbonization process of phenol resin was investigated and observed through an XRD analysis.

This result suggests that during the carbonization (process) step of bulk graphite and C/C composite manufacturing when a phenolic resin is used as a binder, the crystallinity of the binder can be controlled by varying the heating rate. This means that a field engineer may determine an appropriate heating rate for carbonization according to the properties required for a product.

It should be noted that the crystallinity analysis method applied to transform a carbon-based material via a heat treatment can be very useful in many areas. In several studies during which the crystallinity of a carbon material was analyzed by XRD, a quantitative analysis of the interlayer spacing and the

Table 1. Summarization of the interlayer spacing, L_c and L_a , of the phenolic resin-derived carbon powder

Heating rate ($^\circ\text{C}/\text{min}$)	LDCC			MDCC			10/		
	2θ	d_{002} (\AA)	L_c (\AA)	2θ	d_{002} (\AA)	L_c (\AA)	2θ	d_{10} (\AA)	L_a (\AA)
1	19.66	4.51	12.2	24.62	3.61	13.7	43.58	2.08	52.2
5	18.09	4.90	12.2	24.04	3.70	12.2	43.58	2.08	47.1
10	18.88	4.70	13.2	24.13	3.69	13.1	43.49	2.08	47.2
15	19.64	4.52	11.0	24.16	3.68	13.1	43.41	2.08	51.0
20	19.01	4.67	11.0	24.08	3.69	12.6	43.66	2.07	44.7

LDCC, less developed crystalline carbon; MDCC more developed crystalline carbon.

crystal size was attempted with respect to the individual bands obtained after decomposing the (002) peak [10,11,16]. Particularly, Honda et al. [11] measured the variation of the crystallinity during the graphitization of bulk carbon which had been carbonized previously from a phenolic resin. Honda et al. [11] decomposed the (002) peak, which is dependent on the graphitization temperature, into three bands, and systematically measured the interlayer spacing, L_c , and L_a values of the individual bands.

Conflicts of Interest

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

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