J Mater Sci (2007) 42:2076–2080
DOI 10.1007/s10853-006-1213-2

Carbonization behavior of L-tryptophan and gluten

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Received: 27 October 2005 / Accepted: 27 January 2006 / Published online: 9 December 2006

Abstracts Carbonization behavior of L-tryptophan and gluten has been investigated in comparison with that of acenaphthylene using CHN elemental analysis, wide angle X-ray diffractometry, laser Raman spectroscopy and polarizing light microscopy. The carbon derived from L-tryptophan by the heat-treatment at 3,000 °C showed almost the same degree of graphitization as that from acenaphthylene and the average interlayer spacings of both these carbons approached to 0.3354 nm. The average interlayer spacing of the carbon from gluten, on the other hand, did not approach to this value at 3,000 °C. The crystallites in the carbon from L-tryptophan were smaller than those in the carbon from acenaphthylene but larger than those in the carbon from gluten. The ratio, R, of the intensity of the Raman band at 1,360 cm^{-1} against that at 1,580 cm^{-1} and the half width, $\Delta\lambda$, of the Raman band at 1,580 cm^{-1} were measured. The R and $\Delta\lambda$ are the measures for the degree of graphitization. Those values for the carbon from L-tryptophan were nearly equal to those for the carbon from acenaphthylene and smaller than those for the carbon from gluten. The thin film of L-tryptophan heat-treated at 500 °C for 2 h showed a texture consisting of a fine mosaic mesophase structure and an anisotropic flow-type texture of mesophase.

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Introduction

Pitches and cokes, the heavy fractions of petroleum and coal, are two major starting materials of various carbons such as carbon blacks, carbon fibers and activated carbons. Their carbonization behavior and the properties of the resulting carbons have been studied extensively. In contrast, very little attention has been paid to the carbonization behavior of natural resources, for example, proteins or amino acids. Among natural resources, wheat is one of the most productive cereals and gluten is a fraction of wheat protein. The main amino acid composition of gluten is glutamic acid [1]. L-tryptophan is a kind of essential amino acid to a human being and contained slightly in various kinds of proteins (Fig. 1). In previous papers [2, 3], the carbonization behavior of some amino acids and gluten has been investigated and it has been found out that gluten and L-tryptophan carbonize via liquid phase carbonization. The phases in which the pyrolysis reactions proceed have significant implication on the degree of graphitization. The crystallites in carbons derived from L-tryptophan at heat-treatment temperatures (HTTs) up to 1,400 °C were larger than those in the carbons from cellulose and some other amino acids.

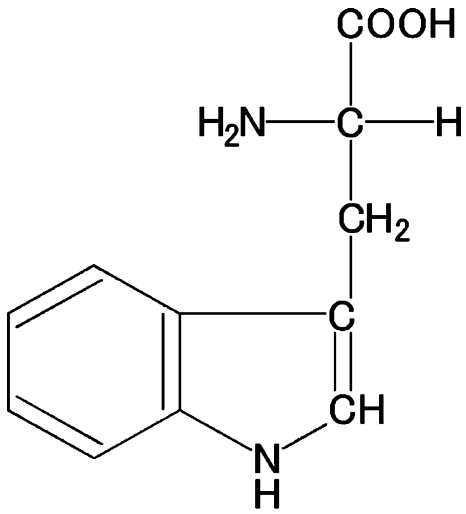

Fig. 1 Molecular structural formula of L-tryptophan

In the present paper, carbonization behavior of gluten and L-tryptophan in the range of HTT up to 3,000 °C has been investigated using CHN elemental analysis, wide angle X-ray diffractometry, laser Raman spectroscopy and polarizing light microscopy.

Experimental

Materials

L-tryptophan, acenaphthylene and gluten, which were all laboratory grade, were purchased from Wako chemical co. and used as the starting materials of carbons. Acenaphthylene from which mesophase pitch and carbon fibers can be produced [4, 5] was used for reference.

Heat-treatment

The starting materials of 1.5–2 g were heat-treated in an electric furnace (CT-40, Advantec co.) having a uniform temperature zone of about 60 mm. During heat-treatment, nitrogen gas flowed through the furnace at a rate of 1 L min^{-1} at atmospheric pressure. The samples were heated at a rate of 10 °C min^{-1}, kept at desired HTTs from 300 to 1,400 °C for 15 min and cooled to room temperature. Some of the samples heat-treated at 1,400 °C were further heated from room temperature to 3,000 °C in 140 min, kept at 3,000 °C for 30 min and cooled to room temperature using an electric furnace (SCC-U-120/203/135, Kurata Gizyutu co.) and under argon gas flow. The carbon samples obtained are listed in Table 1 with their codes used throughout the present paper.

Table 1 Starting materials and maximum HTTs of carbons

Sample code	Starting material	Maximum HTT, °C
TRY1400	L-tryptophan	1,400
TRY3000	L-tryptophan	3,000
GLU1400	Gluten	1,400
GLU3000	Gluten	3,000
ACE1400	Acenaphthylene	1,400
ACE3000	Acenaphthylene	3,000

CHN elemental analysis

The elemental compositions of C, H and N were measured using an organic elemental analyzer (MT-6, Yanako Bunseki Kogyou co.).

X-ray diffraction

Wide-angle X-ray diffraction was carried out on the isotropic samples which were obtained by grinding the carbons and mixing with the high-purity silicon powder as an inner standard. The X-ray source was CuKα radiation.

The degree of graphitization, P1, defined as the probability for the adjacent hexagonal carbon layers to have the positional correlation in graphite was determined from the Fourier coefficients of both 101 and 112 diffraction profiles [6, 7] which were measured using a step-scanning technique with a step of 0.01 and an accumulation time of 30 s. The average interlayer spacing was calculated with Bragg equation from the peak diffraction angles of the carbons determined by referring to the diffraction of the silicon standard. The average interlayer spacings determined from 002, 004 and 006 diffraction are denoted as $d_{002}(002)$, $d_{002}(004)$ and $d_{002}(006)$, respectively. The crystallite sizes parallel and perpendicular to the c-axis, Lc and La, were calculated from the full-widths at half-maximum of the diffraction peaks of the carbons which were corrected for the instrumental peak broadening by referring to the diffractions of the silicon standard. The size parameters determined from 002, 004, 006 and 110 diffractions using Scherrer equation are denoted as Lc(002), Lc(004), Lc(006) and La(110), respectively. For the samples which do not produce the 112 diffraction, the crystallite size perpendicular to the c-axis, La(11), was determined from the 11 diffraction using the Warren equation. The standard deviation of the distribution in the interlayer spacing, σ_c, and the true crystallite size, L_o, were determined using the Hosemann's equation [8].

$$[1/\mathrm{Lc}(00l)]^2 = [1/L_o\,]^2 + \pi^4\,\sigma_c^4\,l^4\,/[16d_{002}(004)^6] \quad (1)$$

where l is the order of diffraction.

Laser Raman spectroscopy

In the Raman spectra of the carbons, the band at 1,580 cm^{-1} is assigned to the E_{2g} mode of the graphite lattice whereas the band at 1,360 cm^{-1} is assigned to the A_{1g} mode which becomes Raman active when the crystal size is finite [9]. The ratio, R, of the intensity of the band at 1,360 c m^{-1} against that at 1,580 cm^{-1}, therefore, relates to the degree of graphitization, the ratio of the basal planes to the edge planes [10] and the concentration of the lattice defects in the graphite structure [11]. The R value decreases as the glass-like carbon structure changes into the graphite structure [12]. The half width, $\Delta\lambda$, of the band at 1,580 cm^{-1} is also a measure of the degree of graphitization [10]. Raman spectra of the carbons were measured with a laser Raman spectrophotometer (JRS-SYS 2000KKW, Nippon denshi co.) equipped with a photo-counting detector using a 514 nm argon-ion laser. The laser beam was incident perpendicularly to the sample surface and the back scattering was detected.

Polarizing light microscopy

The texture of L-tryptophan film was observed using a polarizing light microscope (BX60, Olympus co.) equipped with a hot stage (MS-P1R, Shinkuriko co.). L-tryptophan crystals placed between two cover glasses were heated on the hot stage from room temperature to about 500 °C at a rate of 10 °C min^{-1}, kept at 500 °C for 2 h and rapidly cooled to room temperature. During this process, nitrogen gas flowed over a top cover glass to keep an inert atmosphere around the material and to purge the pyrolysis gases. During the heating process, the L-tryptophan crystals melted and a thin liquid layer was formed between the cover glasses. During the cooling process, this layer was solidified and the thin film was obtained. This film was observed with the polarizing light microscope.

Results and discussion

The degree of graphitization P1, the average interlayer spacing, the standard deviation of the distribution in the interlayer spacing, σ_c and the crystallite sizes of the carbons from L-tryptophan, gluten and acenaphthylene are summarized in Table 2. The P1 value of the carbon from L-tryptophan, TRY3000 was almost equal to the value for the carbon from acenaphthylene, ACE3000. With the carbon from gluten, the broad 10 and 11 diffraction peaks did not split into the 101 and the 100 peaks and the 110 and the 112 peaks, respectively, even at a HTT of 3,000 °C, and P1 value of GLU3000 was close to zero. The $d_{002}(002)$ value of TRY1400 is rather smaller than that of ACE1400 and reached to 0.3371 nm when HTT was elevated to 3,000 °C. The $d_{002}(002)$ value of the carbon from gluten, on the contrary, decreased only from 0.3495 to 0.3428 nm corresponding to the increase in HTT from 1,400 to 3,000 °C. It has been reported that the carbon materials with $d_{002}(002)$ values larger than 0.342 nm tend to show the turbostratic structure [13]. From the absence of the *hkl* diffractions showing three-dimensional regularity and the $d_{002}(002)$ value for GLU3000, it is considered that the crystallites in this carbon have the turbostratic structure.

The Lc(002) value of the carbon from L-tryptophan increased from 5 to 47 nm when HTT was increased from 1,400 to 3,000 °C. The Lc values of TRY3000, however, were much smaller than those of ACE3000 and comparable to those of the cokes heat-treated above 3,000 °C [14, 15]. The values of Lc(002), Lc(004) and Lc(006) decrease with increasing order of the diffractions that were used for the determination of the crystallite sizes for both TRY3000 and ACE3000. This

Table 2 Crystallite structure of carbons

Sample code	TRY1400	TRY3000	GLU1400	GLU3000	ACE1400	ACE3000
P1	–	0.57	–	0.04	–	0.53
d002(002), nm	0.3420	0.3371	0.3495	0.3428	0.3448	0.3361
d002(004), nm	–	0.3369	–	–	–	0.3361
d002(006), nm	–	0.3370	–	–	–	0.3362
Lc(002), nm	5	47	3	6	5	134
Lc(004), nm	–	28	–	–	–	78
Lc(006), nm	–	15	–	–	–	41
La(110), nm	–	69	–	7	–	161
σ_c, nm	–	0.005	–	–	–	0.003
L_0, nm	–	45	–	–	–	138

can be attributed to the distribution in the interlayer spacings. There are two modes of the distribution in the interlayer spacings. One mode is that the stacking of the carbon layers in each crystallite has the disorder of the second kind. In this case, the standard deviation of the distribution in the interlayer spacings, σ_c, and the true crystallite size, L_o, can be determined from the slope and the intercept of the plots of $[1/Lc(00l)]^2$ against the fourth power of the order of diffraction according to Eq. (1). Another mode is that the stacking of the carbon layers in each crystallite is regular whereas the interlayer spacings vary between different crystallites. In this case, the structural strain of the crystallites, ε, and the true crystallite size, L_o, can be determined from the slope and the intercept of the plots of $1/Lc(00l)$ against the order of diffraction [16]. In order to examine the validity of these two assumptions concerning to the mode of distribution, the structural parameters were determined from two different plots corresponding to respective assumptions. As a result, it was found that the latter mode is improper since the plots of $1/Lc(00l)$ against the order of diffraction gave negative intercept. Therefore, it is suggested that the stacking of the carbon layers in these carbons has the disorder of the second kind. The values of σ_c and L_o determined for TRY3000 and ACE3000 are shown in Table 2. The value of σ_c for TRY3000 was in the range of that of ACE3000 whereas the value of L_0 for TRY3000 was smaller than that of ACE3000. With respect to the carbon from gluten, the Lc(002) value only slightly increased from 3 to 6 nm corresponding to the increase in HTT from 1,400 to 3,000 °C. In addition, the La(11) value of GLU3000 was only 7 nm. These results indicate that the crystallite growth both parallel and perpendicular to the c-axis is impeded for the carbon from gluten.

The relative mass of the carbon obtained at 1,400 °C against the mass of the starting material was higher for L-tryptophan than for gluten and these values for L-tryptophan, gluten and acenaphthylene were approximately 16%, 11% and 20%, respectively. Table 3 shows the results of CHN elemental analysis for the carbons from L-tryptophan and gluten with HTTs from 300 to 3,000 °C. At the temperatures up to 1,400 °C, the carbon from L-tryptophan shows larger nitrogen contents than the carbon from gluten. The nitrogen content in the carbon from L-tryptophan amounts to 12% even at 800 °C, then reduces remarkably to ca. 3% at 1,400 °C and gets below the detectable level at 3,000 °C. The nitrogen content of gluten also gets below the detectable level at 3,000 °C. The investigation of the structure of the carbon film from Kapton carried out by Inagaki et al. has shown that the structure development is strongly impeded by the nitrogen still contained in the carbon layers at 2,200 °C but suddenly promoted above 2,300 °C which is the onset temperature of the nitrogen extraction from the carbon layers [17]. Similar effect of the nitrogen can be expected also for the carbon from L-tryptophan and the sudden structure development caused by the increase of HTT from 1,400 to 3,000 °C can be attributed the removal of the nitrogen from the carbon layers.

The values of R and $\Delta\lambda$ for the carbons heat-treated at 3,000 °C are shown in Table 4. The R value of TRY3000 is smaller than that of GLU3000 and close to that of ACE3000. The R value of natural graphite is about 0.10 [18]. The $\Delta\lambda$ values of TRY3000 and ACE3000 are smaller than that of GLU3000. These results suggest that the carbon from gluten contains many structural defects bringing the hexagonal lattice asymmetry and the degree of graphitization of GLU3000 is lower than that of TRY3000 which is comparable to that of ACE3000.

Figure 2a and b are the polarizing transmitted light micrographs of the thin film of L-tryptophan heat-treated at 500 °C. Fine mosaic mesophase structures were observed under the crossed Nicol position (Fig. 2a). Moreover, anisotropic flow-type texture of mesophase was also observed nearby (Fig. 2b). It is possible that high modulus carbon fibers can be derived

Table 4 Half width, $\Delta\lambda$, of the band at 1,580 c m^{-1} and the ratio, R, of the intensity of the band at 1,360 c m^{-1} against that at 1,580 c m^{-1}, calculated from Raman spectra for carbon samples heat-treated at 3,000 °C

Sample code	TRY3000	GLU3000	ACE3000
$\Delta\lambda$, cm^{-1}	21.4	31.8	23.0
R	0.09	0.37	0.10

Table 3 Contents of C, H and N in carbons

HTT, °C		Control	300	350	400	500	800	1,400	3,000
Gluten	C, %	48.4	64.1	66.6	66.1	65.6	71.5	88.7	98.6
	H, %	6.5	6.0	5.1	4.3	3.0	1.5	0.5	0.4
	N, %	13.2	14.1	13.5	12.4	12.4	11.6	1.8	0.0
L-tryptophan	C, %	66.5	73.3	77.9	79.9	78.7	80.7	96.0	99.2
	H, %	6.1	6.0	5.0	4.1	3.2	1.3	0.5	0.6
	N, %	14.0	15.1	14.7	13.9	13.7	12.0	3.2	0.0

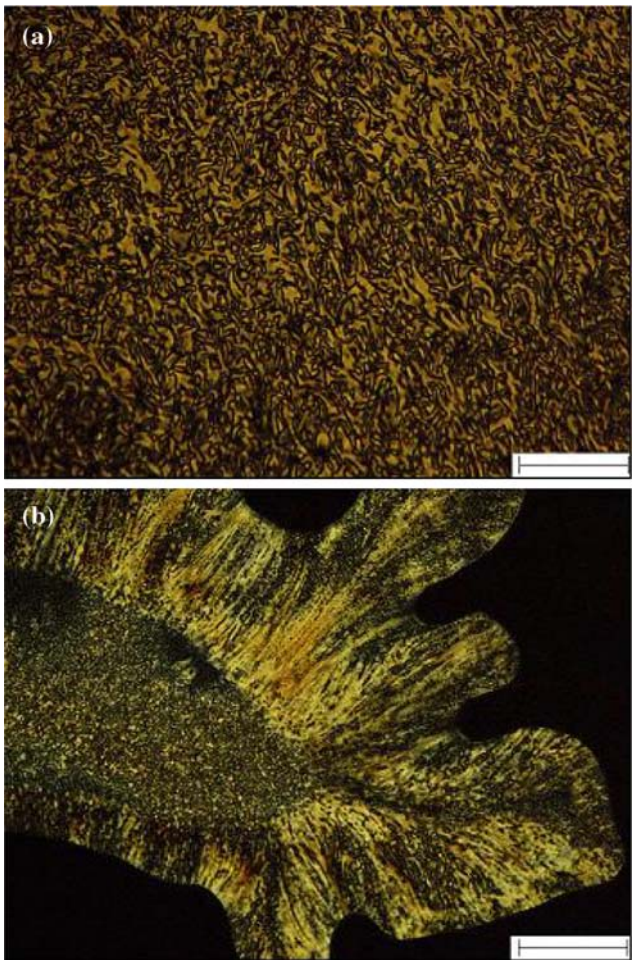

Fig. 2 Polarizing transmitted light micrographs of thin film of L-tryptophan heat-treated at 500 °C for 2 h representing (**a**) fine mosaic mesophase structures and (**b**) anisotropic flow-type texture of mesophase. Scale bars correspond to 50 μm

from L-tryptophan if such mesophase can be oriented by the melt spinning similarly in a case of commercial pitch based carbon fiber.

Conclusions

The carbonization behavior of gluten and L-tryptophan in the range of HTT up to 3,000 °C was investigated and the following conclusions were derived.

1. For the carbon from gluten, the crystallite growth parallel and perpendicular to the c-axis was suppressed. Gluten has a certain potential as a starting material for glass-like carbon.
2. For the carbon from L-tryptophan, the degree of graphitization at 3,000 °C was comparable but the crystallite sizes were smaller as compared with the carbon from acenaphthylene. The crystallite sizes of L-tryptophan heat-treated at 3,000 °C were in the range of the sizes for cokes. L-tryptophan is a candidate of the starting material for graphitizable carbon.

Acknowledgement The authors would like to express great thanks to Mr. H. Wakisaka of Industrial Research Institute of Shiga Prefecture for his help in CHN elemental analysis.

References

1. Bushuk W, C.W. Wrigley (1995) In: Westport CT (ed) Wheat : production and utilization, Avi Pub.Co., p 129
2. Nishikawa G, Kawahara Y, Shioya M, Kimura T (2003) Sen'i Gakkaishi 59:163
3. Nishikawa G, Kawahara Y, Shioya M, Kimura T (2004) ibid 60:105
4. Edstrom T, Lewis IC, Mitchell CV US Patent 3574653, 1971
5. Singer LS US Patent 4005183, 1977
6. Houska CR, Warren BE (1954) J Appl Phys 25:1503
7. Noda T, Iwatsuki M, Inagaki M (1966) Tanso 47:14
8. Shioya M, Takaku A (1989) ibid 139:189
9. Tuinstra F, Koenig JL (1970) J Chem Phys 35:1126
10. Katagiri G (1996) Tanso 175:304
11. Nakamizo M, Honda H, Inagaki M, Hishiyama Y (1977) Carbon 15:295
12. Nakamizo M, Kammereck R, Walker PL Jr. (1974) ibid 12:259
13. Inagaki M, Oberlin M, Noda T (1975) ibid 81:68
14. Noda T, Inagaki M, Fujisawa N (1961) Kogyokagaku 64:1518
15. Iwashita N, Inagaki M (1993) Carbon 31:1107
16. Mizushima S (1968) Tanso 52:9
17. Inagaki M, Tachikawa H, Nakahashi T (1998) Carbon 36:1021
18. Nakamizo M, Honda H, Inagaki M (1978) ibid 16:281