Effect of iodine treatment on morphological control in carbonization of polysaccharides

Naoya Miyajima [a],*, Naoto Ishikawa [a], Hideto Sakane [b], Osamu Tanaike [c], Hiroaki Hatori [c], Takashi Akatsu [d], Eiichi Yasuda [d]

[a] *Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-3-11 Takeda, Kofu, Yamanashi 400-8511, Japan*
[b] *Center for Instrumental Analysis, University of Yamanashi, 4-3-11 Takeda, Kofu, Yamanashi 400-8511, Japan*
[c] *National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan*
[d] *Material and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8503, Japan*

ARTICLE INFO

ABSTRACT

An iodine treatment was applied to control the morphology in carbonization of polymer films prepared from two kinds of polysaccharides, starch and chitosan. Differences in carbonization properties of the films with or without the iodine treatment were investigated by nitrogen adsorption, TG-Mass and Raman spectroscopy. Microporous carbon film was derived from the starch film with iodine stabilization, while non-porous one was done from the chitosan film without iodine stabilization. The char from the starch film was doubled in yield by the iodine treatment but that from the chitosan film remained almost unchanged. It is suggested that these differences in their carbonizations are attributed to the difference in the reactivity between each polysaccharide and iodine, which depends on their polymer conformations.

1. Introduction

Stabilization process is necessary to control the morphology of carbon materials fabricated from thermoplastic resources such as pitch or polyacryronitrile (PAN). Oxygen (air-blowing) is used industrially as the stabilizing process for pitch. Recently, iodine has been proposed as new stabilizer since it can modify pitch easily and rapidly at lower temperatures than oxygen [1]. The iodine treatment improves the thermal stability of pitch in the following mechanism [2–5]; pitch components become large molecules through forming of charge–transfer complexes with iodine and/or promoting of dehydropolymerization, and then pitch is stabilized by preventing its decomposition. Moreover, this modified pitch can be converted to carbons with significant higher char yield than 90 wt% [1]. These effects of the iodine treatment have been applied to other some carbon precursors, such as polyvinyl alcohol [6], polyacetylene [7], mesophase pitch [8], silk fibroin [9] and wood [10]. It is noticed that iodine treatment is only the way to synthesize porous carbon from wood-based precursors without any other activation processes [10].

Polysaccharides are composed of monosaccharide units and the most abundant hydrocarbon resource on the earth. Since the crystallinities and the molecular orientations of some polysaccharides can be easily controlled by chemical or physical modifications, one can tailor it to desired shapes such as fiber, film or more complicated ones. If the as-formed shapes of polysaccharide precursor are kept unchanged after carbonization, one can expect development of novel carbon products from raw biomass materials with highly controlled morphology. Iodine stabilization must be useful for carbonizing such polysaccharides with controlling their thermal stability because they are usually deformed on their decomposition at high temperatures. This approach will be able to inform on new potential applications of polysaccharide resources other than their typical charcoal use.

In this study, stabilization technique using iodine was applied to mold carbon products derived from polysaccharides. Carbon films from two kinds of polysaccharides were prepared and the effects of iodine treatment on their carbonization process were investigated.

2. Experimental

Commercial available potato starch powders or chitosan ones (Kanto Chemical Co., Inc.) were used as starting materials of film precursor. Starch was dissolved in distilled water, and chitosan was

---

* Corresponding author. Tel.: +81 55 220 8545; fax: +81 55 220 8545.
E-mail address: miyajima@yamanashi.ac.jp (N. Miyajima).

dissolved in aqueous acetic acid of 2 vol%. The concentrations of polymer in the solutions were 5 wt%. The starch solution was casted on a glass plate after the gelatinization at 90 °C. The chitosan solution was casted as is on a glass plate because of its appropriate viscosity. They were dried for an overnight at 50 °C in a hot oven and placed in a desicator with a suitable humidity (50 RH). Finally transparent film samples of c.a. 0.8 mm in thickness were obtained and will be referred hereafter as STR or CTS for potato starch or chitosan films, respectively. These films were cut to 10 mm × 10 mm for following experiments.

The films were treated with iodine at 100–150 °C for 24 h in a closed vessel in which the films and excess of iodine were placed far apart. The iodine-treated films were carbonized at 800–1000 °C under nitrogen gas flow. The heating rate was 10 °C/min and the retention time at the final temperature was 1 h. As-filmed STR and CTS were also carbonized with the same heating conditions. The morphological changes of the iodine-treated films before and after the carbonization were observed. The microstructures of the carbonized specimens were observed by scanning electron microscope (SEM, JSM-6500F, JEOL, Ltd.) of Center for Instrumental Analysis, University of Yamanashi. The char yields were evaluated from the weight change of the films after carbonizations. TG and TG-Mass (TG: TGA-50, Rigaku, TG-Mass: QP1100EX, Shimadzu) analysis were attempted to investigate the thermal decomposition behavior of the films samples. Nitrogen adsorption isotherms at −196 °C were measured by volumetric method (BELSORP-28SA, Bel Japan Inc.) to estimate the sample porosity. Raman spectroscopy (NRS-2100, JASCO Co.) was achieved to characterize the iodine-treated films using a 488 nm Ar+ laser of 0.3 mW/cm².

3. Results and discussion

3.1. Carbonization of starch film

Fig. 1 shows the changes of the iodine content and the char yield at 800 °C carbonization of starch film as function of the iodine
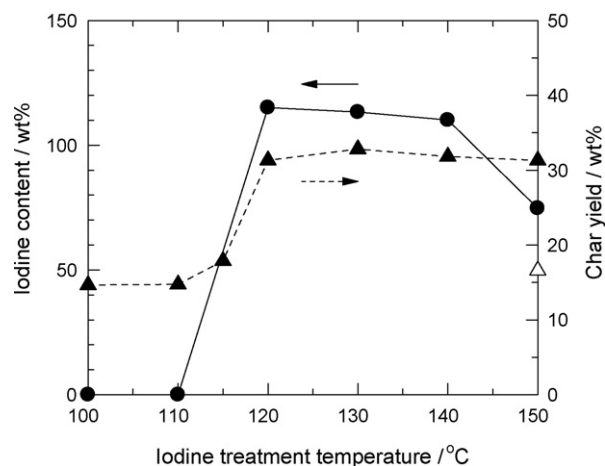

Fig. 1. Iodine content (●) and char yield at 800 °C carbonization (▲, △) of starch film as function of the iodine treatment temperature. (▲) Iodine-treated, (△) heat-treated at 150 °C without iodine.

treatment temperature. The iodine content in the STR was estimated from the weight increase on the iodine treatment. Almost no change in the weight of the film was observed after the heat treatment at 100–150 °C without iodine in the vessel. Iodine content in the STR increased steeply up to about 90 wt% by the iodine treatment at 120 °C or above, while it did not increase below 110 °C. The appearance of the STR iodine-treated ones over 120 °C showed a slight unevenness and deep blue color. The turning point of the char yield coincides with that of the iodine content. The char yields could be approximately doubled by treating the STR with iodine at 120–150 °C, while those of the STR as-filmed and treated at 120 °C or higher for 24 h without iodine were about 15 wt%. Iodine content remained in the carbonized STR is estimated to be small enough, because after carbonization it was already confirmed to be only 2 wt% or less by elemental analysis using iodine-treated pitch [3].
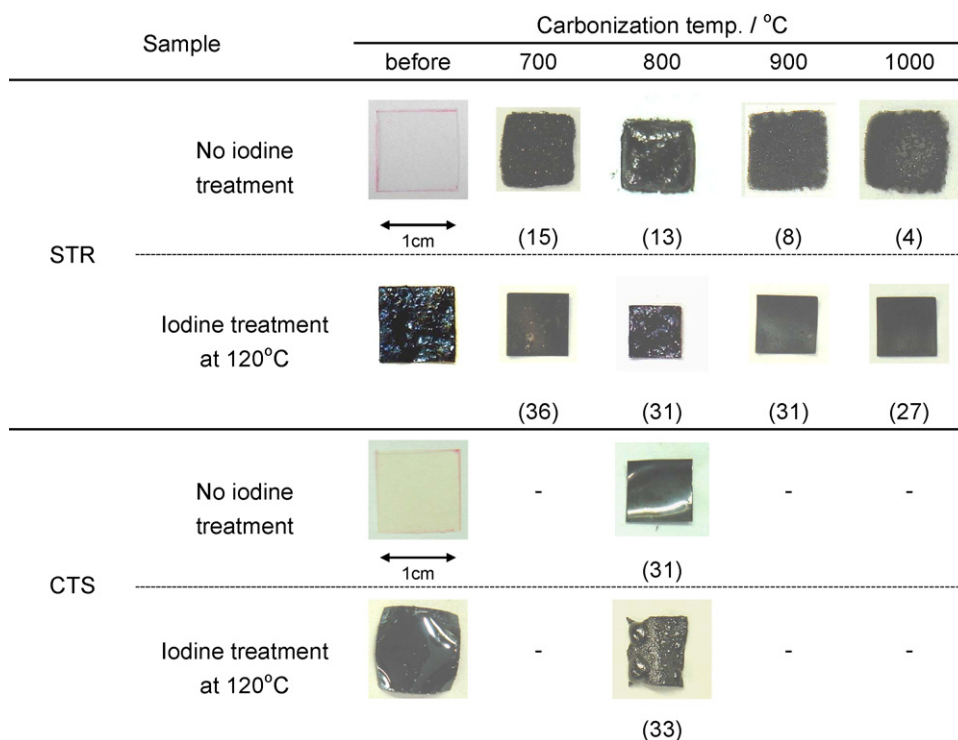

Sample		Carbonization temp. / °C				
		before	700	800	900	1000
STR	No iodine treatment	1cm	(15)	(13)	(8)	(4)
	Iodine treatment at 120°C		(36)	(31)	(31)	(27)
CTS	No iodine treatment	1cm	-	(31)	-	-
	Iodine treatment at 120°C		-	(33)	-	-

Fig. 2. Morphological changes of STR and CTS before and after carbonization. Values in parentheses indicate the char yields in wt%.

Table 1
Porosity parameters determined from N_2 adsorption isotherms.

Sample	Carbonized temperature (°C)	A_{micro} (m²/g)	V_{tot} (ml/g)	W_{ave} (nm)
Original STR	700	305	0.09	0.76
	800	213	0.05	0.76
	900	272	0.09	0.79
	1000	187	0.04	0.76
Iodine-treated STR	700	650	0.22	0.70
	800	596	0.21	0.76
	900	578	0.21	0.76
	1000	524	0.19	0.76

A_{micro}: micropore surface area, V_{tot}: total pore volume, and W_{ave}: average pore width.

These results emphasize that the high char yield of the iodine-treated STR was achieved not by the residual iodine in the treated STR nor the heating effect during the iodine treatment but by the stabilization of iodine.

Fig. 2 shows the morphological changes of the STR and the iodine-treated STR at 120 °C after the carbonization at various temperatures. (The results of CTS are also shown and will be explained in the next section.) The as-filmed STR expanded like a sponge and became extremely fragile after the carbonizations. On the other hand, the iodine-treated STR kept its film shape in all carbonized temperature regions but thermal shrinkages were happened. Their char yields were also kept about 30 wt% in all carbonization temperatures. The STR iodine-treated at 150 °C showed almost same morphological changes and the char yield as those at 120 °C. Then, the temperature of 120 °C is enough for iodine treatment to stabilize the STR and following results will be reported for the STR iodine-treated at 120 °C.

Fig. 3 shows the SEM photographs of the carbonized STR at 800 °C. A number of large void spaces (diameters > 100 μm) surrounded by the carbon matrix are seen in the as-filmed STR but the iodine treatment prevents STR film from developing such large voids during the carbonization. Then, the carbonization of the iodine-treated STR results in the formation of dense carbon film with uneven surface like a crater (Fig. 3(C)).

Fig. 4(A) shows the N_2 adsorption isotherms at −196 °C of the STR carbonized at various temperatures. The carbons derived from the as-filmed STR show Type I isotherms in IUPAC classification, indicating their developments of microporous structure in the products. The increase in N_2 adsorption at $P/P_0 \approx 1$ in Fig. 3(A) must be corresponded to the existence of the macropores or large voids. Though the isotherms of the carbons derived from the iodine-treated STR are also classified as Type I, they have smaller increases in N_2 adsorption at $P/P_0 \approx 1$ than those for as-filmed. This means that there are less large voids for the iodine-treated STR. It is interesting that the adsorptions of N_2 nearby $P/P_0 = 0$ for them are larger than those for the as-filmed STR carbons, which indicates more micropores were developed for the iodine-treated ones. Similar results were described in ref. [10]. Consequently, microporous carbon films could be easily prepared by the iodine stabilization of STR without any other activations.

Porosity parameters, micropore surface area (A_{micro}) and micropore volume (V_{micro}), were calculated by α_s method [11] from these isotherms and summarized in Table 1. Average pore width (W_{ave}) was geometrically calculated by assuming that microporous structure in carbon micro-texture is slit-shaped with carbon hexagonal galleries. As expected from the isotherms, A_{micro} and V_{micro} for the iodine-treated STR are larger than those for the as-filmed one in all carbonized temperatures. They become about twice for the carbonization at 700 °C. These increasings of micropore seem to be related to the increase in char yield shown in Fig. 2. In contrast to A_{micro} and V_{micro}, W_{ave} takes almost the same value of 0.76 nm for all carbons. It is suggested that the micropores caused not by exhaust

of gaseous iodine compounds but by exhaust of pyrolyzed components from starch. The micropores could exist inside the carbon matrix. Their forming mechanism is under consideration.

Results of TG and Mass spectra for the iodine-treated STR at 120 °C for 24 h are shown in Figs. 5(A) and 6. The values in parentheses in Fig. 6 indicate the relative intensities to that of the total ion chromatogram (TIC). The as-filmed STR shows a drastic weight loss around 350 °C and the residual yield at 800 °C is about 10 wt%. The thermal behavior of the iodine-treated STR is obviously different from that of the as-filmed one. The weight decrease gradually continues until about 650 °C and more amount of the residues remains at 800 °C. Some pyrolysis gases such as H_2O, CO and CO_2 are detected around 350 °C as well as the large weight loss in the as-filmed STR. The fragment of $m/z = 60$ at this temperature is characteristic to levoglucosan, that is one of the tar components produced through the decomposition of glucose structures [12,13]. Fragments with similar mass numbers to those of as-filmed STR were also detected for the iodine-treated STR. However, they were observed from lower carbonization temperatures than 350 °C and any fragments of $m/z = 60$ or larger mass numbers corresponding to tar components do not appear during the carbonization. In contrast, the fragments due to iodine species, viz. $m/z = 254$ and 128, are observed mainly at under 600 °C and not at above 700 °C, which implies that iodine does not remain in the carbon products obtained over 700 °C. Therefore, these fragments correspond to the vaporization of physically adsorbed I_2 (i.e., condensation on the film surface) and removal of HI, respectively. HI removal can be an evidence of dehydrogenation.

3.2. Carbonization of chitosan film

According to the results from STR, the CTS was also treated with iodine at 120 °C for 24 h. Fig. 2 also shows the morphological changes and the char yields of the CTSs with the iodine treatment and the carbonization at 800 °C. A film-shaped carbon product with a relatively high char yield, c.a. 30 wt%, could be obtained from the as-filmed CTS. The appearance of the CTS after the iodine treatment became slightly curved with deep blue color. The iodine content of the CTS was 260 wt% that was larger than that of the STR. The smoothness of its surface was lost after the carbonization. It was partly expanded by the release of volatile components from the film inside during the carbonization. The enhancement of char yield by the iodine treatment was small for the CTS, i.e., only 2 wt% increasing.

Fig. 4(B) shows the N_2 adsorption isotherms at −196 °C of the carbonized CTS. The isotherms for the as-filmed CTS carbonized up to 800 °C were classified into Type III that shows a convex curve over the whole relative pressure range. The isotherm was slightly changed to Type II by carbonizing over 900 °C. The BET specific surface area, however, was only 30 m²/g or less, hence the carbonized CTS can be regarded as non-porous from the N_2 gas adsorption behavior. The carbon derived from the iodine-treated CTS was also
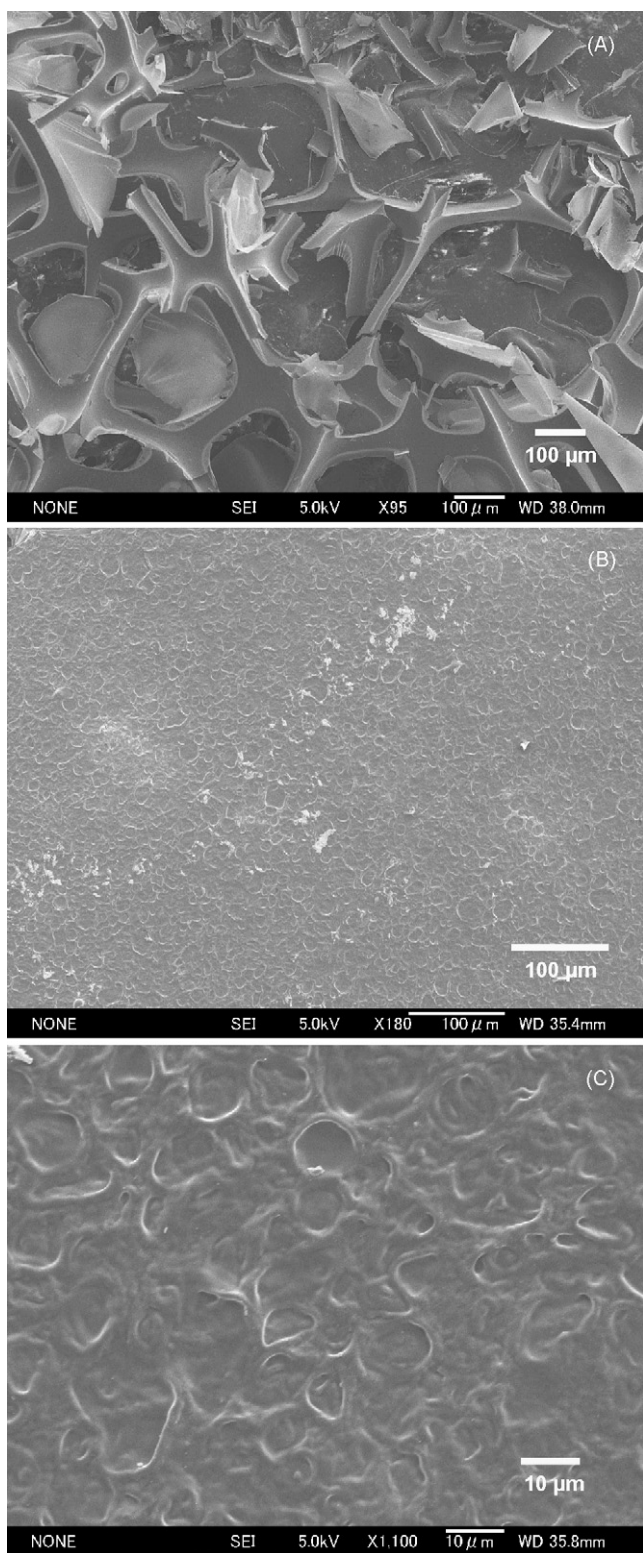
Fig. 3. SEM photographs of the surface of STR carbonized at 800 °C. (A) No iodine treatment STR, (B) and (C) iodine-treated STR.
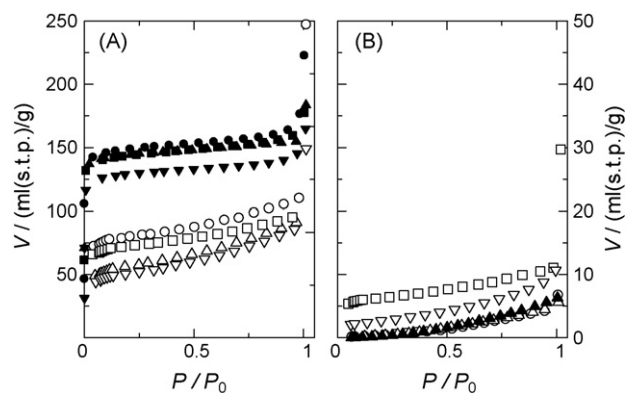

Fig. 4. N_2 adsorption isotherms at −196 °C of STR (A) and CTS (B) films carbonized at various temperatures. (●) and (○) carbonized at 700 °C, (▲) and (△) carbonized at 800 °C, (■) and (□) carbonized at 900 °C, (▼) and (▽) carbonized at 1000 °C. Open marks: as-filmed, closed marks: iodine-treated.
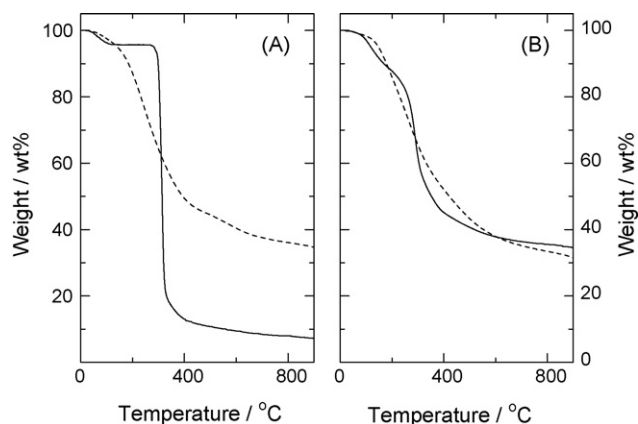

Fig. 5. TG curves of STR (A) and CTS (B). Solid lines: as-filmed, dashed lines: iodine-treated.
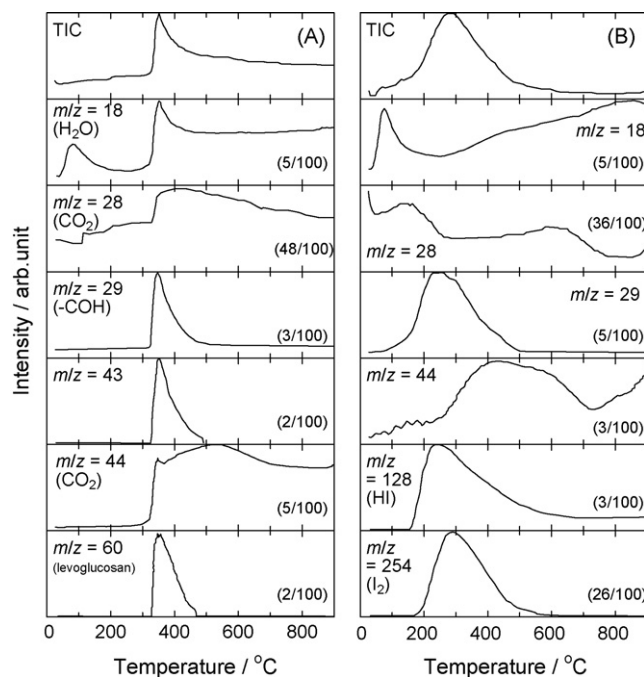

Fig. 6. TG-mass chromatograms of as-filmed (A) and iodine-treated (B) STR during carbonization. Values in parentheses are relative ordinate scale to TIC.

regarded as a non-porous material because of its Type III isotherm. Namely, the CTS could not be converted into a porous carbon even if it was treated with iodine. This is a significant difference from the effect of iodine stabilization on carbonization of STR.

Figs. 5(B) and 7 show the TG results and mass spectra for the iodine-treated CTS. The iodine-treated CTS showed a similar TG
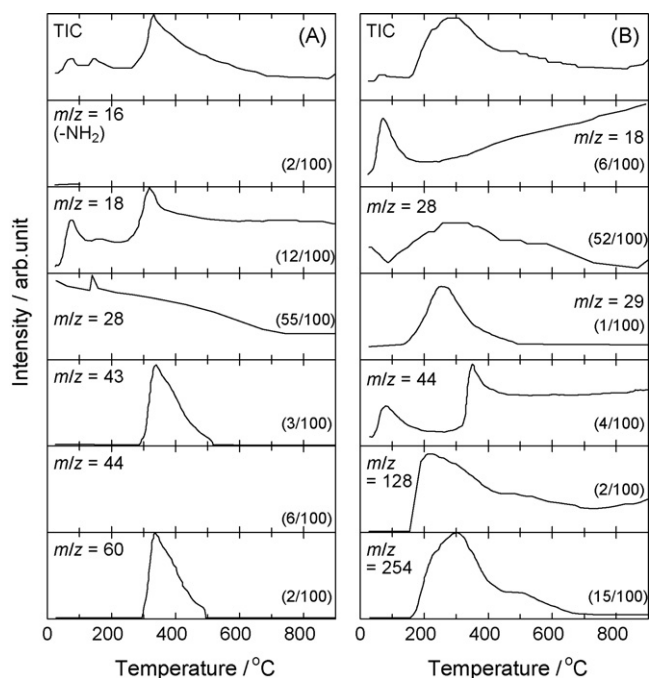
Fig. 7. TG-mass chromatograms of as-filmed (A) and iodine-treated (B) CTS during carbonization. Values in parentheses are relative ordinate scale to TIC.

Fig. 8. Raman spectra of iodine-treated STR and CTS.

curve to that of the iodine-treated STR, but its weight loss is not so largely changed from that of the as-filmed CTS compared with the case of STR. The detected mass numbers of fragments in the spectrum of as-filmed CTS are almost same as those of the as-filmed STR. That suggests that pyrolysis of the CTS proceeds in the same manner as that of the as-filmed STR. The amino group fragment of $m/z = 16$ is detected, however, among the whole range of the carbonization temperatures. Nitrogen atoms still remain in the CTS at relatively high temperature. This would be the reason why the CTS gave high char yields. Although the signal of HI removal is also observed for the iodine-treated CTS, its intensity is smaller than that for the iodine-treated STR.

3.3. Reactivity with iodine and polysaccharides

Fig. 8 shows Raman spectra for the iodine-treated films. It is well known that amylose, the liner chain component of starch, forms helix and a charge–transfer complex with iodine if it is processed with iodide [14,15]. The structure of the complex has been characterized by many researchers using Raman spectroscopy [14–19]. The amylose–iodine complex usually shows two fundamental peaks at 110–115 cm^{-1} (weak) and 165–168 cm^{-1} (strong) and their overtones. They are generally assigned to I_3^- and I_5^- (I_2 associated with I_3^-), respectively. In the present results, characteristic peaks at similar shifts around 110 cm^{-1} and 169 cm^{-1} are observed from the iodine-treated STR. The amylose–iodine complexes with two types of polyiodine ions are formed in the iodine-treated STR. On the other hand, the Raman peak around 110 cm^{-1} is stronger in the iodine-treated CTS than around 169 cm^{-1}. It implies iodine mainly exists as I_3^- in the complex with CTS.

From the results of the Raman spectra and the TG-Mass spectra, the stabilization reaction proposed for the iodine-pitch system [4,5] proceeds in the iodine-STR and -CTS ones. The reaction contains the thermal stabilization and/or dehydropolymerization of the monosaccharide units through forming charge–transfer complexes with iodine in their iodine-treated films. Some gas evaporations
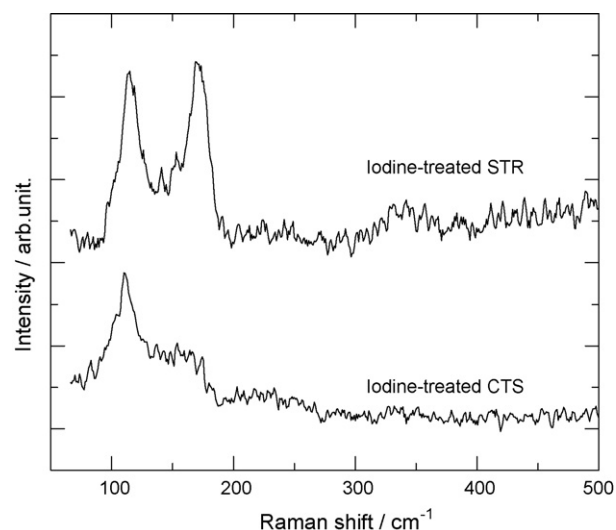
such as dehydration accompanied by the dehydropolymerization occur in the lower temperatures of the carbonization for the iodine-treated films than those for non-treated ones. There was the difference, however, in the efficiency of char yield or the porosity by the iodine stabilization between the STR and the CTS. This difference seems to be related to the conformation in both polysaccharides. Starch has an elastic helical structure owing to its α-glucoside bonding of monosaccharide units, in which iodine atoms are present as a one-dimensional chain [15]. In the iodine-pitch complex, iodine molecules form a stacking (sandwich) structure with pitch components [3]. Iodine is fully surrounded by the organic component (starch or pitch) in the complexes. Therefore, the iodine stabilization would be successfully carried out for starch in the similar manner of the iodine-pitch system.

In contrast to starch, chitosan has an extended two-fold helical conformation, that is, a rigid linear like structure, since it consists of β-glucoside bonding of glucosamine unit as seen for cellulose (poly-β-(1, 4)-D-glucose) [20,21]. Nakamura et al. reported that the iodine treatment of cellulose shows only 4 wt% increase in the char yields and a slight increase in the surface area of micropores for the carbonization [10]. Chitosan in the present paper also shows similar results on char yield to cellulose in the iodine stabilization. Moreover, Raman spectrum of the iodine-treated cellulose resembles that of the iodine-treated CTS in this study. That indicates the same interaction with iodine between these two polysaccharides. They also concluded that iodine has an ionic charge as I_3^- in the iodine–cellulose complex. From the results, chitosan and cellulose with rigid conformation seem to surround iodine incompletely. Though the actual structure of iodine–chitosan complex has not been detailed yet, it is possibly suggested that the ionic iodine such as I_3^- mainly reacts with the amino groups in the chitosan. It is presumed that the chitosan polymers are locally or partially oxidized by iodine, which leads to the less stabilization. In addition, the original high char yield in the CTS without iodine treatment may make the effect of iodine treatment on char yield relatively small.

Because all amino groups are directed to the outside in the two-fold helical conformation [20], iodine molecules can adsorb physically subsequently around I_3^-. This would be why the iodine content for the iodine-treated CTS is larger than that for the iodine-treated STR. Consequently, the CTSs tend to be expanded by the release of large amount of physisorbed iodine from the film inside during the carbonization.

4. Conclusions

In order to develop new carbon products with highly controlled morphology from raw biomass materials, iodine stabilization technique was attempted to two kinds of polysaccharide films, potato starch and chitosan.

In starch, microporous carbon films could be synthesized through the iodine stabilization. The char yield and the micropore volume could be doubled by the iodine treatment. Non-porous carbon films were obtained by carbonization of the chitosan film without iodine treatment. The film surface of carbonized chitosan film with iodine treatment became ragged because of release of volatile iodine compounds from the film inside during the carbonization. Both polymers have the similar molecular structure but have the different polymer conformation. The conformations lead to the differences in the reactivity with iodine and the subsequent stabilization.

Acknowledgements

References

[1] H. Kajiura, Y. Tanabe, E. Yasuda, A. Kaihou, I. Shioda, S. Yamada, J. Mater. Res. 13 (1998) 302–307.
[2] H. Kajiura, Y. Tanabe, E. Yasuda, Carbon 35 (1997) 169–174.
[3] N. Miyajima, T. Akatsu, T. Ikoma, O. Ito, B. Rand, Y. Tanabe, E. Yasuda, Carbon 39 (2000) 1831–1837.
[4] N. Miyajima, T. Akatsu, T.O. Ito, R. Sakuravs, S. Shimizu, M. Sakai, Y. Tanabe, E. Yasuda, Carbon 39 (2001) 647–653.
[5] Y. Tanabe, F. Tanaka, M. Takahashi, T. Iiyama, N. Miyajima, S. Fujisawa, E. Yasuda, Carbon 42 (2004) 1555–1564.
[6] S. Mukuruma, H. Oki, M. Shiotani, J. Yamanshita, JP, Patent 2004-339627 (2004) (in Japanese).
[7] M. Kyotani, S. Matsushita, T. Nagai, Y. Matsui, M. Shimomura, A. Kaito, K. Akagi, J. Am. Chem. Soc. 130 (2008) 10880–10881.
[8] J. Sasanobe, A. Oba, T. Nakamura, JP Patent 1-314734 (1989) (in Japanese).
[9] M.R. Md. Khan, Y. Gotoh, H. Morikawa, M. Miura, Y. Fujimori, M. Nagura, Carbon 45 (2007) 1035–1042.
[10] K. Nakamura, Y. Tanabe, Y. Nagakura, T. Nisizawa, K. Fukuyama, Y. Hatakeyama, E. Yasuda, TANSO 234 (2008) 215–219.
[11] K. Kanko, C. Ishii, T. Rybolt, Characterization of Porous Solids III, Elsevier, Amsterdam, 1994 (p. 583).
[12] T. Hirata, M. Maekawa, T. Nohmi, J. Mass Spectr. Soc. Jpn. 46 (1998) 2595–3274 (in Japanese).
[13] N. Miyajima, S. Shinji, T. Suzuki, H. Sakane, Mater. Sci. Eng. B 148 (2008) 249–252.
[14] R.C. Teitelbaum, S.T. Ruby, T.J. Marks, J. Am. Chem. Soc. 100 (1978) 3215–3217.
[15] R.C. Teitelbaum, S.T. Ruby, T.J. Marks, J. Am. Chem. Soc. 102 (1980) 3322–3328.
[16] X. Yu, C. Houtman, R.H. Atalla, Carbohyd. Res. 292 (1996) 129–141.
[17] A. Sengupta, M. Holtz, E.L. Quitevis, Chem. Phys. Lett. 263 (1996) 25–32.
[18] N.A. AL-Hashimi, K.A. Hassan, El-M. Nour, Spectrochim. Acta A 62 (2005) 317–321.
[19] I. Jerman, V. Jovanovski, A. Šurca, S.B. Hočevar, M. Gaberšček, A. Jesih, B. Orel, Electrochim. Acta 53 (2008) 2281–2288.
[20] Japanese Society for Chitin and Chitosan, Application of chitin and chitosan, GIHODO SHUPPAN, Tokyo (1990) (in Japanese).
[21] T. Sakajiri, T. Kikuchi, I. Simon, K. Uchida, T. Yamamura, T. Ishii, H. Yajima, J. Mol. Struct.: THEOCHEM 764 (2006) 133–140.