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Electron Beam Effects on Lignin Stabilization during Carbonization

Byoung-Min Lee, Phil-Hyun Kang and Joon-Pyo Jeun*

Research Division for Industry & Environment, Korea Atomic Energy Research Institute,
Jeongeup 580-185, Korea

Abstract - Lignin can be a valuable natural chemical resource. Structurally, lignin is a three-dimensional polymer made up of condensed C-C bonds and some ether linkages, most of which are not readily degraded. In this study, lignin carbonization under various electron beam pretreatment conditions was characterized through a thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Raman spectroscopy. Lignin stabilization was controlled by various doses of electron beam irradiation corresponding to 50, 100, 200, 500 and 1,000 kGy; the carbonization process was performed under a nitrogen gas atmosphere at 1000°C for 1 h. The TGA results showed that a 1,000 kGy lignin dose increased the residue weight from 39.96% to 45.23%, compared to non-irradiated lignin. This observation is in agreement with the XRD and Raman spectroscopy results, in which the two theta degrees and the degree of crystallization were improved by increasing the electron beam irradiation.

Key words : Electron beam, Lignin, Carbonization, Irradiation

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INTRODUCTION

Lignin is the second most abundant and aromatic rigid biopolymer in the world. Lignin provides mechanical strength and structural support as a matrix component for the structure of lignocellulose chemically bonded with cellulose and hemicellulose. In the paper pulp industries, about 70 million tons year^{-1} lignin as a co-product are generated (Satheesh *et al.* 2009). Lignin is composed of three different phenyl propane monomer units: p-coumaryl, coniferyl and sinapyl alcohol (Thevenot *et al.* 2010; Pandey *et al.* 2011). Structurally, lignin consists of aromatic rings with side chains and -OH and -OCH_3 groups which are linked by various strong covalent bonds such as alkyl-aryl ether and C-C bonds (Hirose *et al.* 2002). Lignin is an amorphous polymer that has grafting and crosslinking abilities. Thus, Lignin has been widely used in polymer composites and adhesive applications and has served as a precursor in the synthesis of carbon and carbon fibers (Hayashi *et al.* 2000; Jin *et al.* 2012; Hainal *et al.* 2012). It is supposed that about 30% of the organic carbon in the earth's biosphere is generated from lignin and lignin structure ensures a high carbon level in the ratio of elements; the high utility of this high carbon content has motivated the application of lignin as a precursor in the production of carbon fibers and carbon nanotubes (Boerjan *et al.* 2003).

An electron beam is composed of a narrow stream of electrons in the form of waves; electron beams are widely used in the medical and polymer industries, pollutant detoxification, food manufacturing, and the agricultural fields (Ragan *et al.* 2011; Imbraguglio *et al.* 2012; Senna *et al.* 2012). In a recent study, electron beam irradiation was used as a physical pretreatment process for bioethanol production. Furthermore, ionizing radiation can easily penetrate the chemical structure of lignin to produce free radicals that can modify the lignin structure and break down dispensable bonds (Gonugunta *et al.* 2012).

In the present study, different absorbed doses of electron

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* Corresponding author: Joon-Pyo Jeun, Tel. +82-62-570-3063, Fax. +82-62-570-3098, E-mail. jpjeun@kaeri.re.kr

beam irradiation were used to study the influence of processing parameters on lignin carbonization. A thermogravimetric analysis (TGA) was used to study the effect on the degree of carbonization in the lignin, depending on the absorbed dose of the electron beam. The crystalline structure of the carbonized lignin was analyzed by X-ray diffraction (XRD) and Raman spectroscopy.

EXPERIMENTALS

Materials

In this study, alkali lignin is used as a starting material for the carbonization. Alkali lignin was purchased from Sigma Aldrich (Mw: 28,000).

Lignin Carbonization

Electron beam irradiation (EBI) was used to stabilize the lignin at EB-tech (Daejeon, Korea). EBI was carried out at the absorbed doses of 50, 100, 200, 500 and 1,000 kGy using a dose rate of 50 kGy scan^{-1} at beam current of 30 mA and beam energy of 1.14 MeV. The electron beam irradiated lignins were carbonized in a tubular furnace for 1 hour after the temperature reached to 1000°C at a heating rate of 10°C min^{-1} from ambient temperature under a nitrogen atmosphere. And then, the tubular furnace was cooled at room temperature.

Characterization

The effect of an electron beam in thermally stabilizing lignin was investigated through a Thermogravimetric analysis (TGA) using a TA Instruments SDT-Q600 at a 10°C min^{-1} heating rate, over a temperature range of 40 to 1000°C by purging nitrogen gas. X-ray diffractometer (XRD, D/MAX-2500, Rigaku) was used to produce x-ray diffractograms of the carbon atoms and to determine the crystalline structure of carbonized lignin. The XRD analysis was carried out over a temperature range of 5° to 80° (2 theta) at a step speed of 3° min^{-1} and a step size of 0.01°. The Raman spectra of the carbonized lignin were recorded with Raman spectrometer (Nanofinder 30, Tokyo Instruments) using 488 nm lasers. The peaks were fitted with Gaussian curves using a linear background obtained from the Raman spectra in the 500 to 2,000 cm^{-1} region.

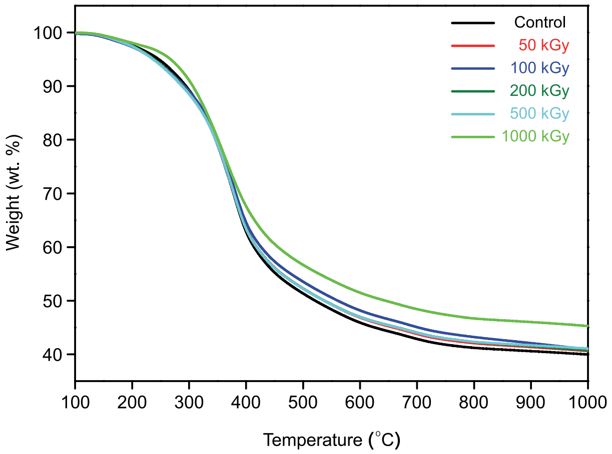

Fig. 1. TGA thermograms measured under nitrogen gas for lignin stabilized at different electron beam irradiation doses.

RESULTS AND DISCUSSION

Thermogravimetric analysis

Fig. 1 shows the thermal properties of stabilized lignin under a nitrogen atmosphere. These results indicate that a large weight loss occurred at approximately 350°C which was mainly due to lignin degradation. Meanwhile, the residue weight increased from 39.96% to 45.23% owing to an increase in the irradiated dose of the electron beam from 0 to 1000 kGy. Before carbonization, the lignin stabilized at doses of 1000 kGy and higher doses improved the thermal stability (Cho *et al.* 2007).

X-ray diffraction analysis

X-ray diffraction analysis can be used to characterize hard carbons and crystal structure. In Fig. 2, The appearance of broad (002) diffraction peak at 22° was evidence for short range ordering of adjacent aromatic rings, which make distribute a preferential interatomic distance between carbon atoms. It can be observed that increasing with absorbed doses of electron beam irradiation leads to gradually increase the intensities of (002) diffraction peak. This indicates that the electron beam irradiation has been attributed to the existence of both of highly ordered graphite and less ordered graphite (Jones *et al.* 1991).

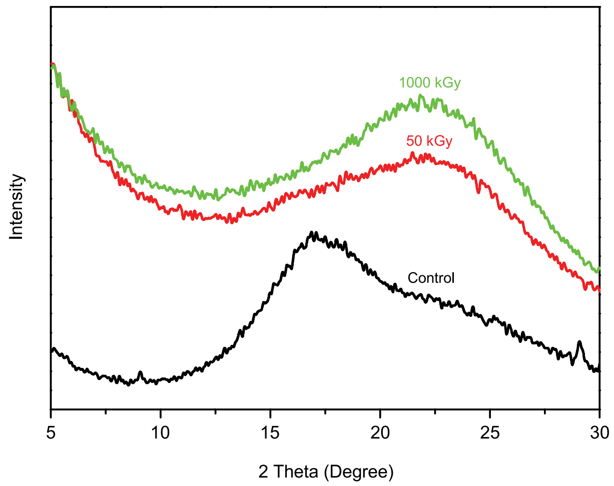

Fig. 2. X-ray diffractograms for carbonized lignin at 1000°C at heating rates of 10° min^{-1} following stabilization by an electron beam.

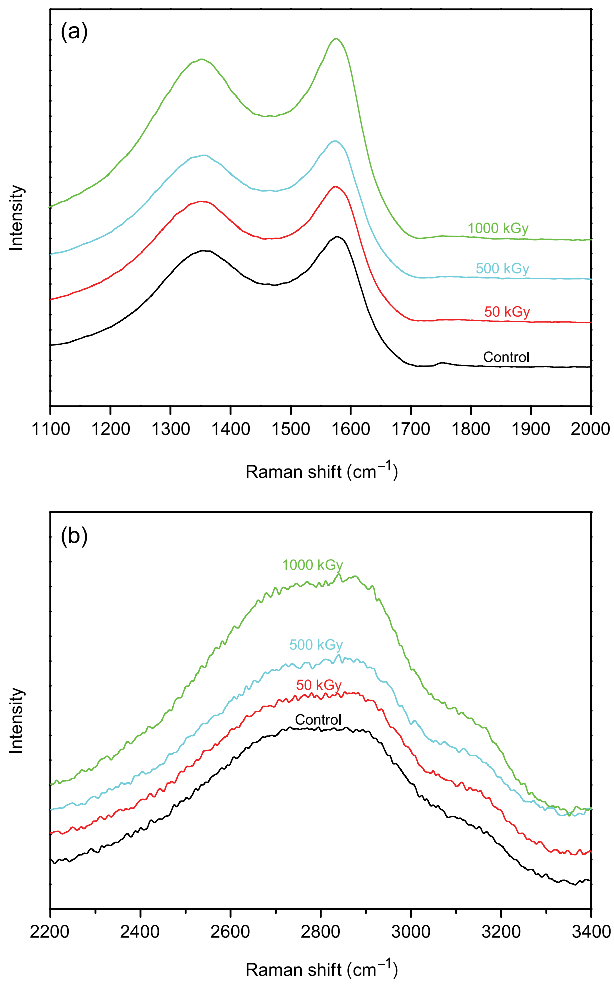

Fig. 3. Raman spectra of carbonized lignin in (A) the first-order region and (B) the second-order region, under the same conditions as in Fig. 2.

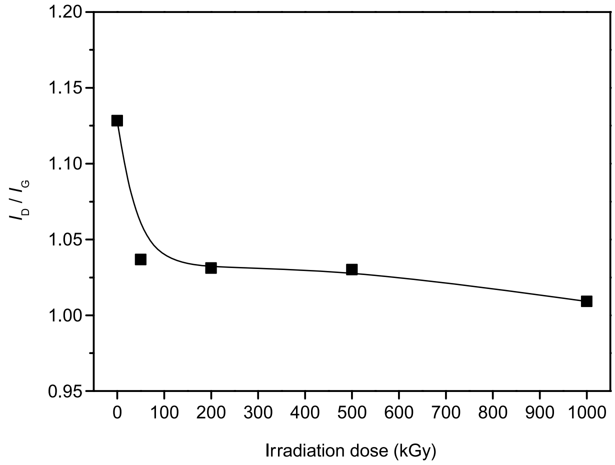

Fig. 4. The ratio of the intensity of the D-band versus the intensity of the G-band from the raman spectra of carbonized lignin under the same conditions as in Fig. 2.

Raman spectra

Raman spectrometry is used to characterize a carbon material because of the drastically spectral changes not only due to the kind of available allotropic carbon but the well-defined structural changes of the each allotrope. Raman spectra of the carbonized lignin are shown in Fig. 3. In general, two sharp peaks of G-band around 1,580 cm^{-1} and D-band around 1,350 cm^{-1} were appeared in carbon materials. The first-order region of the Raman spectrum at approximately 1,580 cm^{-1} (G-band) can be attributed to the E_{2g} mode of the graphite lattice vibration. The D-band appeared at approximately 1,350 cm^{-1}, corresponding to the A_{ig} vibration mode, which can be attributed to lattice defects, edges of graphite layers, and structurally disordered carbons (Kim *et al.* 2000). The resulting Raman spectra all exhibit bands at approximately 1,350 and 1,580 cm^{-1}; upon increasing the absorbed dose of the electron beam, the 1,350 cm^{-1} band remained almost constant, whereas the 1,580 cm^{-1} band shifted toward a lower frequency. In the second-order region of the spectra, from 2,200 to 3,400 cm^{-1}, carbonized lignin exhibited bands at 2,700 cm^{-1} and 2,900 cm^{-1}, resulting from the change in the absorbed dose are shown in Fig. 3(B). These bands were an over tone of the D′-band and a combination of the D-band and D′-band. Generally, highly crystalline samples cause the band at 2,700 cm^{-1} to split into two bands. The spectra were used to calculate the intensity ratio of the D to G-band (I_D/I_G), which decreased with an increase of the stabilization absorbed dose of the electron beam (Fig. 4). Thus, radiation treatment resulted in a decrease in the disorder amount and number of defects (Rodriguez-Mirasol *et al.* 1996; Ishimaru *et al.* 2007; Panapoy *et al.* 2008; Song *et al.* 2009).

CONCLUSION

We reported the effects of electron beam irradiation on the stabilization component of lignin carbonization. TGA results showed that the residue weight of the stabilized lignin increased by approximately 5%, depending on the absorbed dose of the electron beam, as high radiation energy produced thermally stable lignin. During carbonization, the lignin structure transformed from the phenolic compound to graphite in stages depending on the carbonization temperature, caused by the previous electron beam irradiation step. The XRD and Raman analyses indicated that the degree of graphite increased with the amount of electron beam treatment. Remarkable increases in the intensity of the (002) diffraction peaks were observed, and the ratio of the intensity of the D-band to the intensity of the G-band of ratio also increased. The degree of carbonization can be easily controlled by electron beam irradiation.

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