Chemical and Micro-Structural Changes in Glass-Like Carbon during High Temperature Heat Treatment

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Abstract: A glass-like carbon was fabricated using furan resin. The influence of heat treatment temperature during fabrication process on the chemical and micro-structural changes was studied by various analytical and spectroscopic methods including TGA, FT-IR, CHN, TEM and XRD. The chemical resistance properties of the fabricated glass-like carbon were also investigated. It has been found that the heat-treated samples at higher temperature up to 2600 °C in N_2 atmosphere had little weight loss, small amounts of functional groups, and high carbon content. The fabricated glass-like carbons upon heat treatment at 2600 °C showed an amorphous stage without any grain growth and/or reconstruction of structure. The glass-like carbon had much better chemical resistance than the artificial graphite, and exhibited a high chemical resistance due to its low surface areas, minimum impurities, and low graphite crystallites.

Keywords: glass-like carbon, microstructure, transmission electron microscopy, X-ray diffraction.

Introduction

Glass-like carbons have been developed as commercially available products in the early 1960's under the designations of "Glassy Carbon" and "Vitreous Carbon".[1-3] The glass-like carbons can be obtained by the pyrolysis of thermosetting resin such as phenolic resin, furan resin or celluose.[4-7] Although the detailed preparation process significantly varies, glass-like carbons from different sources appear to have similar properties.[8] The physical properties of the glass-like carbon including low density, chemical inertness, closed porosity, thermal stability, impermeability to gases and liquids, electrical conductivity and glass-like isotropic properties allow its application in the aerospace, medical, mechanical, chemical, semiconductor industries.[5, 8-14] The apparent density of commercially available glass-like carbons ranges from 1.46-1.50 g/cm^3 (2.27 g/cm^3 for a single crystal graphite) irrespective of heat treatment temperature, indicating the existence of thermally stable closed pores in the matrix.[5,8,15] The microstructure of glass-like carbon contains a significant volume of pores as indicated by its low density.[15] The high temperature structural stability is displayed as a strong resistance to graphitization and crystallite growth.[4,7,8] There are at least three models that have been introduced to explain the structure of glass-like carbon. The first model, proposed in 1972 by Jenkins and Kawamura[8,16,17] is called the ribbon-stacking model. This model describes glass-like carbon as a conglomerate of randomly twisted and highly anisotropic graphite fabrils whose width gradually increases due to high temperature heat treatment. The second model, proposed by Oberlin,[16,18] postulates the existence of crumpled graphite-like layers which reduce with heat treatment. The third model, proposed by Shiraishi,[16,19] suggests that a predominance of closed pores in the bulk of glass-like carbon. The high gas impermeability of glass-like carbon is explained well by this

model. These three models however insufficiently explain the glass-like carbon entirely. Consequently, the new structural models of glass-like carbon were suggested.[16]

There have been some reports on the pyrolysis of furan resin to fabricate glass-like carbon, but the information available in the literature is not sufficient to understand the process of carbon atom condensation during the resin pyrolysis.[9] In this study, a furan resin was used to fabricate glass-like carbon to understand the chemical and micro-structural changes during the heat treatment at high temperature up to 2600 °C.

Experimental

Sample Preparation. Furan resin known commercially as KC-5302 (M_w = 2,150, M_n = 190, and viscosity at 25 °C = 170 cPs) of Kangnam Chemical Co. in Korea was used as the carbon precursor. Furan resin samples were catalyzed by the addition of 0.5 wt% of *p*-toluenesulfonic acid monohydrate (PTSA, $CH_3C_6H_4SO_3H \cdot H_2O$, Shinyo Pure Chemical Co. Ltd., Japan). The homogenization of the catalyst in the resin was accomplished by mechanical stirring for 30 min. The catalyzed samples were poured into a borosilicate glass mold and polymerized for five days at room temperature under a pressure of 460 kg$_f$/m^2. The polymerized samples were cured at 100 °C for 96 hrs in a drying oven under a pressure of 460 kg$_f$/m^2 by increasing very slowly up to 100 °C. The samples were soaked for 1 hr after every 5 °C increment during the curing step. The cured samples were buried with fine cokes powders and then carbonized with slowly increasing the temperature from room temperature to 1000 °C at a rate of 1 °C/hr in nitrogen atmosphere. A soaking time of 1 hr was given for every 60 °C increase from room temperature up to 600 °C to give sufficient time to release the gases. Finally, the samples were heat-treated up to 2600 °C and held for 1 hr in Ar gas atmosphere.

Characterizations of Sample. The samples polymerized, cured, carbonized at 1000 °C, and heat-treated at 2600 °C were characterized by several analytical and spectroscopic methods as described below.

TGA, FT-IR and CHN Analyses: A thermo-gravimetric analyzer (STG-SDTA851, Mettler, Switzerland) was used to monitor the mass changes of the samples during the heat treatment process. The samples were heated from room temperature to 900 °C in a flowing air atmosphere (200 mL/min) at a heating rate of 10 °C/min.

The vibrational spectra of the samples were collected using a Fourier Transformed Infrared (FT-IR) spectrometer (MB104, ABB Bomem Inc., Canada) equipped with a diffuse reflectance accessory. Specimens were prepared by mixing the sample with potassium bromide powder.

CHN elemental analysis (CHN-2000, LECO Co., U.S.A.) was carried out to measure the amount of carbon, hydrogen, and nitrogen in the samples by a coal method. The amount

of carbon and hydrogen was measured by infrared absorption technique. The amount of nitrogen was measured by a heat conduction technique.

Microstructure Analysis by TEM and XRD: The microscopic features of the glass-like carbons were observed with a high-resolution transmission electron microscope (HR-TEM, CM200, Philips). HR-TEM images were obtained from amorphous-like regions at a variety of defocus conditions. A transmission electron microscope operating at 200 kV was used to record the TEM image of the samples and selected area diffraction patterns (SADP). TEM samples were prepared in the following methods; disks with a diameter of 3 mm were cut from the fabricated glass-like samples, the disks were mechanically dimpled until the thickness was about 10 micrometers, copper rings were glued to one side of the thinned disks, and these were further thinned using 4 keV Ar$^+$ ions until a tiny hole appeared at the center of the disk.

XRD (XD-D1, Shimadzu Corporation, Japan) measurement was made using CuKα radiation (λ = 1.542 Å) from the powders of the samples: these were cured, carbonized at 1000 °C and then graphitized at 2600 °C. The (002) diffraction profiles of high purity silicon metal powder were used as an internal standard.

Observation of Chemical Resistance: Concentrated HCl, H_2SO_4 and HNO_3 solutions were used to measure the chemical resistance of glass-like carbon. The glass-like carbons were immersed in a mixture of 11.2 mol HCl, 18.3 mol H_2SO_4 and 15.5 mol HNO_3 for two weeks at room temperature. The samples were then washed and dried for the measurement of weight changes and the observation of surface changes in SEM.

Results and Discussion

TGA, FT-IR and CHN Analyses. The pyrolysis behavior of the samples after the consecutive heat treatment processes is shown in Figure 1. The pyrolysis phenomena of the polymerized sample in Figure 1 were almost identical to the results of E. Fitzer *et al.*[1,20] Weight loss did not occur below 200 °C in the cured sample, and it decomposed in the same way as the polymerized sample above 200 °C, even if a difference in the degree of weight loss existed. The carbonized sample showed an abrupt weight loss at 660 °C and the sample heat treated at 2600 °C exhibited a similar weight loss as that obtained at 710 °C in the air atmosphere. The carbonized and heat treated samples at 2600 °C shown in Figure 1 followed the pyrolysis behavior of the general carbonaceous materials. However, these temperatures were higher than the thermal decomposition temperature of the artificial graphite. This is due to the fact that glass-like carbon had a lower surface area, less impurities, and fewer edges in the crystal than that of an artificial graphite.[18]

FT-IR spectra of the samples at different stages from the

raw materials to glass-like carbon are shown in Figure 2. In the mixture of furan resin and PTSA, a band due to bonded -OH absorption appeared at 3400-3550 cm^{-1}. However, this absorption band disappeared after the polymerization step at room temperature. This seems to be due to the promotion of dehydration by PTSA catalyst. This result is in accordance with the thermal analysis of the polymerized sample in Figure 1 in which about 10% of weight loss occurred around 100 °C.

The absorbance bands at 3125 cm^{-1} (C-H stretch), 1510 cm^{-1} (C=C stretch), 1020 cm^{-1} (C-O-C symmetry stretch), and 980 cm^{-1} (C-H out-of-plane deformation) in the furan ring decreased during polymerization step and then further decreased or completely disappeared with the following heat treatment.[21,22] The decrease in the peak intensity upon heat treatment indicates that PTSA accelerates the breaking of furan rings.

The absorbance band intensities at 1020 cm^{-1} (=C-O-C=),
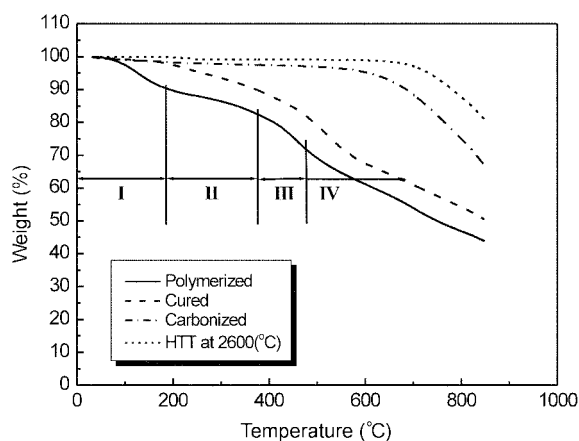
Figure 1. TGA analysis of samples obtained from the consecutive heat treatment processes to make glass-like carbon from furan resin.
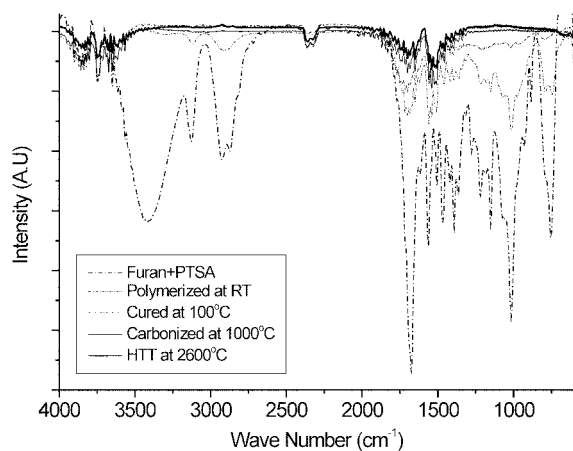
Figure 2. FT-IR spectra of the sample after the consecutive heat treatment steps.

2925 cm^{-1} (CH$_2$ asymmetric stretching), 1725-1730 cm^{-1} (saturated ketone), 1680 cm^{-1} (unsaturated ketone) and 1565-1570 cm^{-1} (C=C stretching) of the furan ring decreased with increase of the thermal treatment temperature.[21] The decrease in the intensities of these vibrational bands may be due to the opening of the furan rings. In the case of methylene group vibration at 2925 cm^{-1} and that for the saturated ketone between 1725-1730 cm^{-1}, the decrease in intensities with heat treatment are due to the elimination of hydrogen and oxygen atoms by opening of the furan ring.[21]

The relative intensities of the unsaturated ketone band and that of C=C of furan ring were compared using the spectra of the cured and polymerized samples. The cured sample showed a relatively higher intensity than the polymerized sample. The higher intensity of the unsaturated ketone band in the cured sample originates from the reaction with oxygen in air during the curing process.

In the FT-IR spectra of the samples heated to temperature 100 °C, a shoulder appears at 1760 cm^{-1}. This band may be ascribed to carboxylic acid or ester. The intensity of band at 1610 cm^{-1} is due to conjugated double bonds or benzene rings.[21] This band also decreased in intensity with increasing heating temperature. Such behavior corresponds to that of the bands at 880 cm^{-1}. In addition, the decrease in intensity of the 790 cm^{-1} band (C-H out-of-plane deformation) is seen in Figure 2.

The absorbance peaks at 1510 cm^{-1} (C=C stretch) and 1680 cm^{-1} (-C=C-C=C-CO-) were shown in the carbonized and HTT at 2600°C samples. This means that the dehydrogenation of aromatic hydrogen is accompanied by increased aromaticity of the structure.

Exothermic reaction of the mixture of furan and PTSA generated H$_2$O which evaporated during the polymerization stage. This phenomenon is confirmed by the decrease of -OH band intensity in the FT-IR spectra of furan and PTSA mixture during polymerization in Figure 2 as well as the weight loss in the polymerized TGA profile of Figure 1 around 100 °C. The rupture of methylene bridges in the furan resin, forming CH$_4$ as a by-product, and the opening of the furan ring as shown in the polymerized and cured spectra of Figure 2, can be explained by the weight loss in regions I and II of Figure 1.

At temperatures above 400 °C (region III: 380 to 480 °C), the reaction of pyrolysis of water with remaining methylene bridges occurred.[20] A secondary reaction, which promotes the formation of keto groups, was recognized by the decrease of water content. In region III, the formation of methane ceased due to the oxidation of the methylene bridges, which then released significant amount of hydrogen. In region IV (above 480 °C), the carbonyl groups liberated CO, leading to a highly unsaturated aromatic C-H residue capable of forming crosslinked aromatic systems.[1] These phenomena in region III and IV, such as the opening of the furan ring and decomposition of organic compounds, occurred during heat treat-

ment and that led to a decrease in intensity of vibrational bands in the FT-IR spectra.

Table I shows the results of CHN analysis after the consecutive heat treatment processes. The amount of oxygen was calculated by subtracting the amounts of C, H and N from the total of 100 percent. The furan resin was composed of 66.7% carbon, 6.3% hydrogen and 27.0% oxygen. After the polymerization of the mixture of furan resin and 0.5% PTSA, the carbon contents increased to 72.4% and oxygen contents decreased to 21.8%. However, the oxygen contents increased after curing. This phenomenon can be explained by the crosslinking of resin mixtures by oxygen in the air during the curing process and this is consistant with the increase of relative intensity in the unsaturated ketone band in FT-IR after the curing process. The carbon contents increased extensively during heat treatment processes. After the heat treatment at 2600 °C, the content of carbon was 100% due to the elimination of the other chemical components by the high temperature heat treatment.

Microstructure Analysis by TEM and XRD. It has been found using relevant lattice fringe images that the glass-like carbon from furan resin has a microstructure of turbostratic stacks of small polynuclear aromatic molecular fragments held together with random orientation by cross-linking through the trigonal carbon bonds. Therefore, a glass-like carbon is noncrystalline and isotropic in structure after carbonization, and consequently it is hard and impervious in property.

Very little microstructural changes occurred with the heat-treatment as shown in Figure 3. It has been suggested that the structural stability of glass-like carbon is due to the tangled geometrical arrangement of the carbon crystallites which prevents crystal growth and recrystallization without massive rearrangement of the structure.[4,7,8] On the other hand, the micropores which are present in the tangled carbon structure can act to slow down the crystallite growth and graphitization by eliminating the contact between adjoining crystallites.[7] This contact is necessary for the adjustment of carbon atoms in one crystallite into registry with those in another crystallite.

It is easily recognized that there is a distinct difference in peak shape between glass-like carbon and polycrystalline metal silicon as shown in Figure 4. In general, all the diffraction patterns obtained after heat treatment were analogous

to the previously reported data.[7,11,13,23] With an increase in heat treatment temperature, the broad (002) and (101) diffraction peak of glass-like carbon gradually shifts to a higher angle side and its peak becomes sharper.

The values of d-spacing and L_c at (002) peak were calculated from Figure 4. The values of $d_{(002)}$ peak of the carbonized and HTT at 2600 °C samples were 3.698 and 3.512 Å, respectively. The crystallite sizes of the samples were 18.858 and 22.150 Å, respectively. The values of d-spacing and L_c of the samples are in the same range compared to the commercialized glass-like carbon.[13,23]

The increase in intensity as well as sharpness of the XRD peak indicates the development of a glass-like carbon crystalline structure. However, the crystallinity of the samples were far from the crystal material, as could be seen from the broadness of the peak.

Chemical Resistance of Glass-Like Carbon. Figure 5 shows the morphological changes of the sample surface after the chemical resistance test. Conventional synthetic graphite was used as a reference sample to compare with the glass-like carbon. In the conventional synthetic graphite, many graphite particles were removed from the surface after the two weeks'
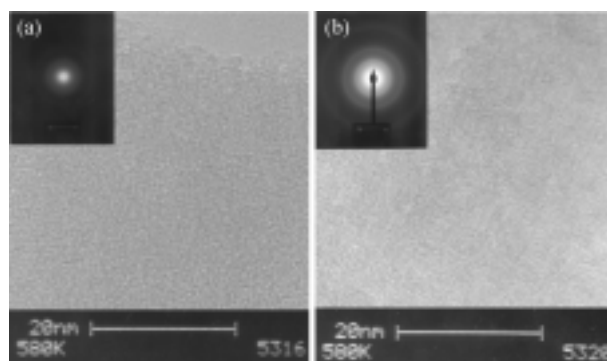
Figure 3. TEM micrographs and electron diffraction patterns of glass-like carbon after heat treatment at (a) 1000 °C and (b) 2600 °C.

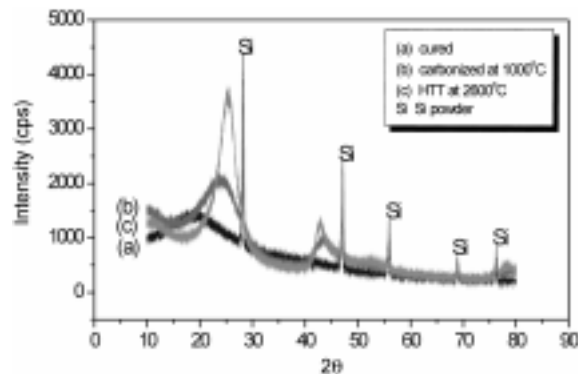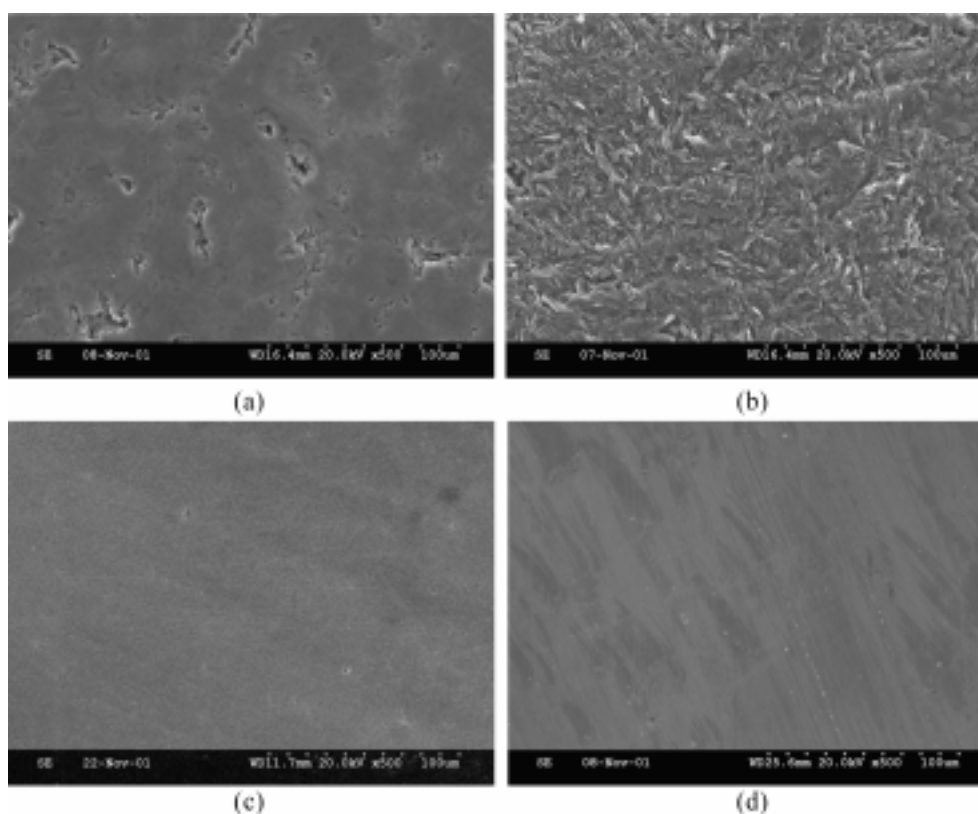**Table I. Results of Carbon, Hydrogen and Nitrogen Elemental Analysis (%)**

	C	H	N	O
Furan Resin	66.7	6.3	0	27.0
Polymerization	72.4	5.8	0	21.8
Curing	62.3	3.7	0	34.0
Carbonization	99.2	0.1	0	0.7
Heat treated at 2600 °C	100	0	0	0

Figure 4. X-ray diffraction patterns of glass-like carbons after the consecutive heat treatment.

Figure 5. SEM micrographs of conventional synthetic graphite surface and glass-like carbon surface heat treated at 2600 °C. (a) conventional synthetic graphite, (b) conventional synthetic graphite after acid treatment, (c) heat treated glass-like carbon at 2600 °C, and (d) heat treated glass-like carbon at 2600 °C after acid treatment.

acid treatment as shown in Figure 5(b). It is known that the conventional synthetic graphite immediately exfoliates into small particles when placed in a mixed solution of sulfuric acid and nitric acid. However, no changes are shown in the surface of glass-like carbon after the same acid treatment. The improved chemical resistance of glass-like carbon can be explained by the lower specific surface area and the smaller amounts of carbon crystallite edges.

Conclusions

The fabrication process and properties of the glass-like carbon derived from furan resin were studied and the following conclusions could be drawn:

1. The pyrolysis mechanism of furan resin was presented in the TGA profiles of the polymerized sample. H_2O was the primary product in region I. The furan ring was opened in region I through III by rupture of the methylene bridges. The carbonyl groups liberated CO, leading to a highly unsaturated aromatic C-H residue forming a crosslinked aromatic system in region IV.

2. FT-IR band intensity decreased with increasing heating temperature. The -OH band at 3400-3550 cm^{-1} was eliminated at the polymerization step. The absorbance of the band

at 3125, 1510, 1020, and 980 cm^{-1} in the furan ring decreased at the polymerization step and further decreased or disappeared with the following heat treatment due to the opening of the furan ring. The intensities of bands at 2925 and 1725-1730 cm^{-1} decreased due to the elimination of hydrogen and oxygen atoms by the opening of the furan ring.

3. TEM and XRD analysis revealed that very little microstructural changes occurred with the heat-treatment. The microstructure of the glass-like carbon had isotropic and amorphous structures without rearrangement of crystals and transformation to graphite structures after the heat treatment at 2600 °C. Structural stability of glass-like carbon is probably due to the tangled geometrical arrangement of the crystallites which prevents crystal growth and recrystallization without massive rearrangement of the structure.

4. The surface structure of glass-like carbon was not so much changed after the chemical resistance test in the mixture of strong acids for two weeks.

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