

Simultaneous TG-DTA/MS Study of Cedar-based Woodceramics for Use in Snowmelt System

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Simultaneous measurement of TG-DTA and EGA using mass spectrometry (TG-DTA/MS) revealed that thermal change of cedar-based woodceramics in helium up to 1273K was initiated by dehydration, which was followed by several gas evolution steps. Evolution of CO₂ was detected mainly throughout the reaction, while benzene, phenol and xylene were slightly observed in the middle temperature region (ca. 573-873K), attributed to adsorbed phenol resin fragments during sintering. Gaseous CO was distinct at higher temperatures (ca.873-1273K) showing progressive carbonization occurring on the sample. The results suggested that the ability of gas absorption of woodceramics is higher than that of carbonized cedar, and characteristic water adsorption effect is observed for coarser samples below 443 K. Furthermore, the results implied the presence of different gas adsorption sites.

Key words: woodceramics, TG-DTA/MS, EGA, cedar, carbon dioxide, gas absorption, hybrid material

1. INTRODUCTION

Woodceramics are porous carbon/carbon composite materials newly developed by carbonizing wood or woody materials impregnated with thermosetting resin, such as phenol resin, in a vacuum furnace [1]. Hence, woodceramics are environmental-friendly or are ecomaterials whose by-products, such as the decomposition products, can be recycled [2].

Very few reports are available concerning thermal studies of woodceramics. Kano et al [3] provided thermogravimetry (TG) and differential thermal analysis (DTA) data on woodceramics based on Hiba. However, the measurement was performed on a relatively large mass of sample, i.e., 25 mg. Since woodceramics undergo change involving gas evolution, smaller sample mass is preferred. Arii and Momota [4] reported the simultaneous measurement of mass spectrometry (MS) with TG-DTA on the same material. TG-DTA/MS is particularly effective for examining the sintering process. It is well known that the physical properties of the woodceramics are controllable by changing the temperature of sintering, and the density as well as the electric resistivity can be therefore controlled. Thus, the development of cedar-based woodceramics sintered at 1073K(800 °C) for use in a domestic snowmelt system is under way. The system is designed to operate at ca. 338K (65 °C).

Accordingly, the thermal change of cedar-based woodceramics differing in particle size (granules to powder) for use in the snowmelt system application was studied by mainly using TG-DTA/GC-MS(Gas chromatography-Mass spectrometry). Particular interest was paid on the gas evolution at temperatures up to 473 K (200°C). Furthermore, TG-DTA for woodceramics on

small mass sample is reported for the first time.

2. EXPERIMENTAL

2.1 Samples

Woodceramics prepared from medium density fiber (MDF) board of cedar impregnated with 55% phenol resin and sintered at 800°C was used. Fig. 1 shows the scanning electron micrograph of the cedar-based woodceramics used in the present study. Although wood fibers are normally about 23 to 30 μm in diameter, acicular morphology about 50 nm in diameter indicates the formation of glassy carbon nano-tubes.

Samples differing in particle size, i.e., powder 250 μm or less in granularity (sample No. 6), granules ranging from 1.0 to 1.7 mm in particle diameter (No. 7), granules 1.7 to 4.0 mm in particle diameter (No. 8), and those larger than 4.0 mm in particle diameter (No. 9) were prepared. Powder of carbonized cedar (~250 μm) was also prepared as comparative sample (No. 5). The samples are given collectively in Table 1.



Fig. 1 SEM photograph of cedar-based woodceramics.

2.2 Simultaneous TG-DTA/GC-MS

Simultaneous TG-DTA/GC-MS measurements were performed on 15 mg each of samples using a TG-DTA TG8120 coupled with QP-5050A (Rigaku Corporation) in the temperature range of from R.T. to 1273 K at a heating rate of 20 Kmin⁻¹ under helium gas flow of 300 mlmin⁻¹, while holding GC-oven temperature and GC-Inj temperature both at 533K, and holding MS-Det temperature and I/F temperature at 573 K.

Separately, TG-DTA measurement in air was performed on the samples, and the results are given in Fig. 7.

3. RESULTS AND DISCUSSION

3.1 Thermal change of as-received samples in inert (He gas) atmosphere

Figure 2 shows the TG-DTG curves of the samples, and the mass losses are summarized in Table 1. Figs. 3 and 4 are the TG-MS curves for carbonized cedar (No.5) and woodceramics (No.6) having the same particle size distribution. In Figs. 3 and 4, TIC represents the total ion current, and the numerals stand for m/z. Although the mass loss seems to proceed monotonously, DTG shows that the thermal change occurs roughly in 3 to 4 stages, and this can be confirmed by TIC in Figs. 3 and 4. The first stage, which may consist of two stages of dehydration and evolution of gaseous carbon dioxide (CO₂), is up to 473 K, the second is from that temperature to ca. 873 K; and the third is temperatures higher than ca. 873 K, at which carbon monoxide (CO) is discharged showing progressive carbonization.

At temperatures ca. 473 K (200°C) or lower, two reactions occur simultaneously and/or successively; gaseous CO₂ (m/z 44) is evolved simultaneously with, or after, dehydration (m/z 18).

Subsequently, in the second stage, gradual mass loss up to ca. 773 K is mainly due to the discharge of gaseous CO₂, but an abrupt gas evolution may take place attributed to the evolution of aromatic compounds, particularly benzene (m/z 78, at ca. 703 K), and others such as toluene, phenol, xylene, or methyl benzene. This is confirmed by gas chromatograph (GC) for gas accumulated at temperatures 473K or higher. It is also confirmed that carbonized cedar evolves species with higher molecular weight, such as naphthalene.

At temperatures ca. 873 K (600°C) or higher, the discharge of CO₂ (m/z 28) decreases as the discharge of CO increases to show progressive carbonization.

Figure 2 and Table 1 read that the total mass loss is smaller for carbonized cedar (No.5), and is larger for samples having wider range of particle size distribution (No. 6 and No.9). However, from the slopes of the TG curve in the temperature range of from ca. 573 K to 773 K, it is presumed that the gas evolution occurs in the same manner for carbonized cedar and for woodceramics No.6 having the same particle size distribution. Thus, this suggests that the gas discharge kinetics is greatly influenced by particle size distribution, and that the discharge mechanism is the same for woodceramics No.6 and carbonized cedar. Referring to Figs. 3 and 4, however, the gas species evolved in the temperature range above are different. Furthermore, it is confirmed from GC that carbonized cedar (No.5)

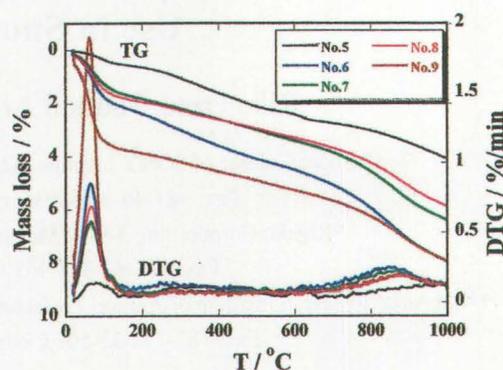


Fig. 2 TG-DTG curves of the samples in He.

Table 1 Samples and mass loss.

| No. | Sample | Granularity | Mass loss to 433K % | Total Mass loss % |
|-----|------------------|--------------|---------------------|-------------------|
| 5 | Carbonized cedar | -250 μ m | 0.57 | 3.88 |
| 6 | Cedar-based WC | -250 μ m | 2.20 | 7.64 |
| 7 | | 1.7-1.0mm | 1.71 | 6.10 |
| 8 | | 4.0-1.7mm | 1.80 | 5.61 |
| 9 | | >4.0mm | 3.76 | 7.58 |

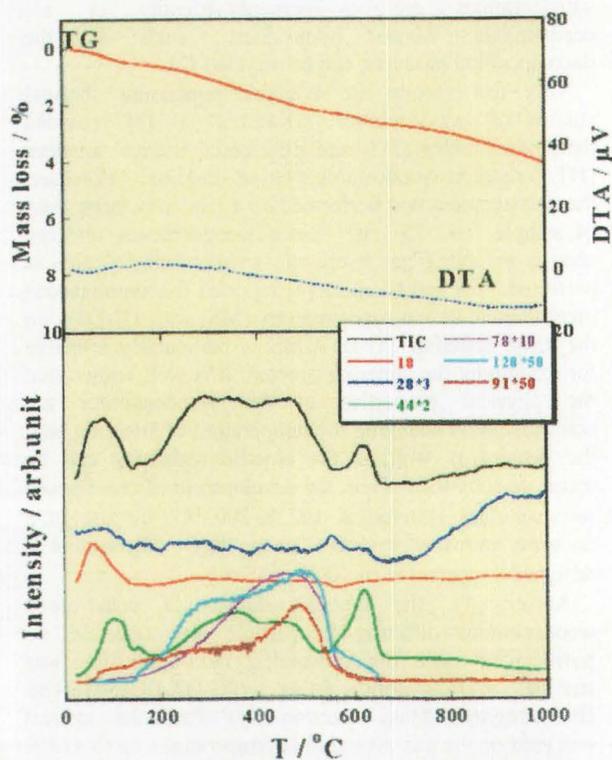


Fig.3 TG-DTA/MS curves of carbonized cedar (-250 μ m; No.5). The numerals in the figure stand for m/z.

evolves gases of higher molecular weight such as naphthalene, but that woodceramics do not. Hence, presumably, the gas discharge mechanism is rather based on physisorption, and not on chemical reaction.

From Figs. 4 and 5, the gas evolution behavior of woodceramics samples differing in particle size can be observed. Although the total mass loss to ca. 1273 K is approximately the same, the gas discharge rate up to 433 K (ca. 160°C) is quite different. That is, coarser sample (No. 9) shows sharp discharge of physically adsorbed water, and this amounts to about half (3.76 %) the amount of total mass loss (7.58 %). This is quite striking, and is characteristic to the coarse sample.

On the other hand, sample consisting of finer particles (No. 6) shows discharge of carbon dioxide over a wide temperature range, and furthermore, shows signals probably suggesting the presence of decomposition fragments of phenol resin, e.g., benzene (m/z 78), toluene (m/z 91), and xylene (m/z 105). Such decomposition products were presumed due to adsorbed to the samples, and rinsing with hot water was performed.

After rinsing with hot water, only signals assigned to water, carbon dioxide, and carbon monoxide (m/z 28) were observed on the mass spectrograms. However, the high water adsorption ratio for the sample larger than 4 mm in particle diameter (No. 9) retained a water adsorption ratio of 1.75 %, with respect to the total mass loss of 6.41 %, while sample No. 8 showed merely 0.95 % of water adsorption with respect to the total mass loss of 5.75 %.

It is characteristic to this cedar-based woodceramics that water adsorption ratio is higher for coarser samples. This is in contrary to general understanding that specific surface area increases with reducing particle size, and that the adsorption ratio increases with increasing specific surface area. However, for cedar-based carbon materials, as shown in Table 2[5], the specific surface area as well as the adsorption ratio increases with increasing particle size. One possible reason might be the anisotropy of this material. As shown in Fig. 1, acicular products develop during sintering, and capillary effect may increase adsorption of water by some capillary effect. However, as the size is reduced, the particles become isotropic, and the capillary function might be lost.

Table 2 Adsorption ratio of cedar based carbon.

| | Iodine adsorption mg/g | Chlorine adsorption mg/g | Specific surface area m ² /g |
|--------------------------------------|---------------------------|-----------------------------|--------------------------------------------|
| Carbonized cedar / μm | | | |
| -63 | 690 | 97.56 | 534 |
| 250-1000 | 765 | 139.39 | 607 |
| Comparative (Commercially available) | | | |
| Active carbon | na | 216.69 | 900-1300 |

Another particular interest is on the evolution of carbon dioxide (CO₂; m/z 44) up to ca. 443 K. Each of woodceramics Nos. 7 to 9 shows a well-distinguished doublet for the evolution of carbon dioxide. This may suggest different adsorption sites

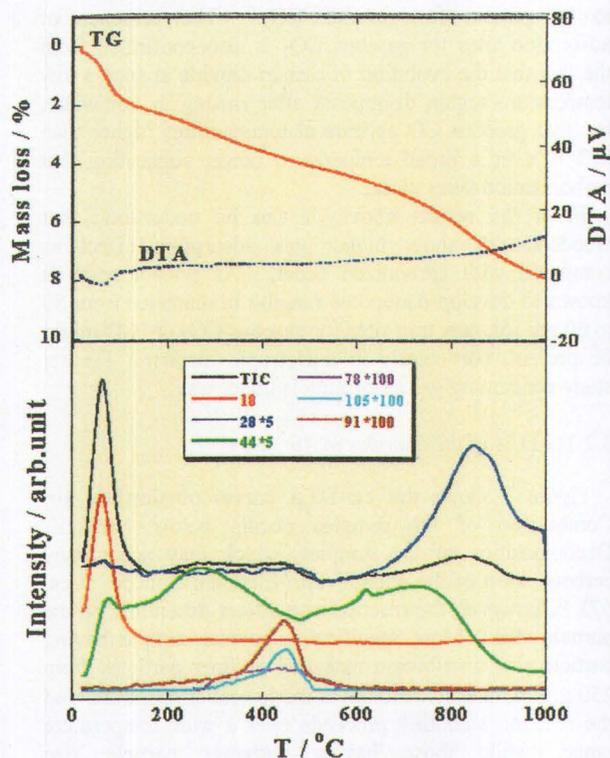


Fig 4 TG-MS curves of cedar-based woodceramics (-250μm; No.6). The numerals in the figure stand for m/z.

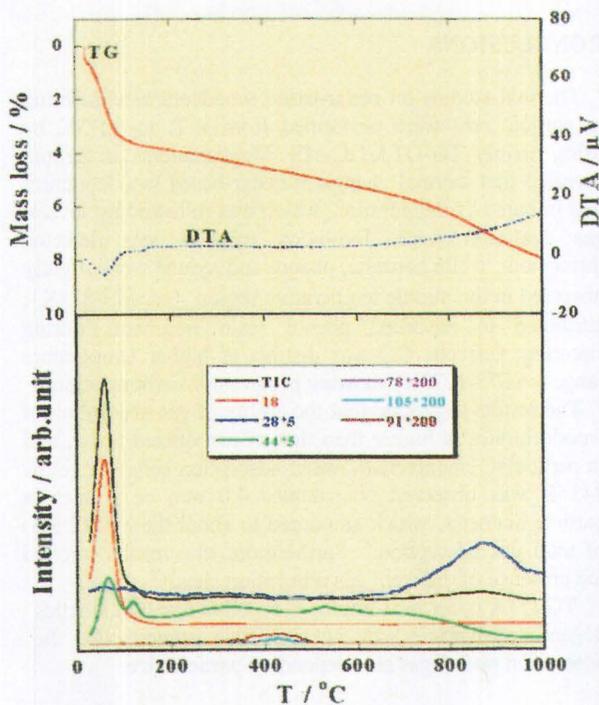


Fig.5 TG-MS curves of cedar-based woodceramics (>4mm; No.9). The numerals in the figure stand for m/z.

to be present for gaseous CO_2 . The presence of adsorption sites for gaseous CO_2 is also confirmed from the fact that the evolution of carbon dioxide at such a low temperature region disappears after rinsing in hot water, but that gaseous CO appears at temperatures higher than 873 K over a broad temperature range, suggesting that carbonization takes place.

From the results above, it can be understood that woodceramics show higher gas adsorption effect as compared with carbonized cedar. As phenol resin is known to develop nanopores ranging in diameter from 50 to 60 nm [6], new trap sites for gaseous CO_2 or H_2O might be present, particularly in anisotropic manner. Further study concerning gas adsorption is under way.

3.2 TG-DTA of the Samples in Air

Figure 7 shows the TG-DTA curves obtained in air. Combustion of the samples occurs below 1073 K. Decomposition of the samples, which may accompany carbonization of the phenol resin fragments, occurs at ca. 673 K, however, the reaction rate differs depending on the particle size. More specifically, powder sample having particle size distribution extended to finer particles from 250 μm initiates its reaction at the lowest temperature, and the reaction smoothly proceeds over a wide temperature range, while those having narrower particle size distribution complete the reaction in a short period of time. Furthermore, particles with distribution on the larger size take longer time for the reaction; i.e., the sample shows an exothermic peak that initiates gradually and takes longer time for the completion of the reaction. This evidences that the reaction kinetics depends on the particle size, and shows self-similar reaction [7].

CONCLUSIONS

Thermal studies on cedar-based woodceramics differing in particle size were performed from R.T. to 1273K by using mainly TG-DTA/GC-MS. Measurements in helium revealed that thermal change of cedar-based woodceramics was initiated by dehydration, which was followed by several gas evolution steps. Evolution of CO_2 was detected throughout, while benzene, phenol and xylene were slightly observed in the middle temperature region (ca. 573-873K), attributed to adsorbed phenol resin fragments during sintering. Gaseous CO was distinct at higher temperature range (ca.873-1273K) showing progressive carbonization.

The results suggested that the ability of gas absorption of woodceramics is higher than that of carbonized cedar, and in particular, characteristic water adsorption behavior below 443 K was observed on samples 4.0 mm or greater in particle diameter, which amounted to about the half (3.5%) of total gas adsorption. Furthermore, the results implied the presence of different gas adsorption sites.

TG-DTA in air for samples shows that reaction kinetics depends on particle size; i.e., this also suggests that the adsorption rate of gas also depend on particle size.

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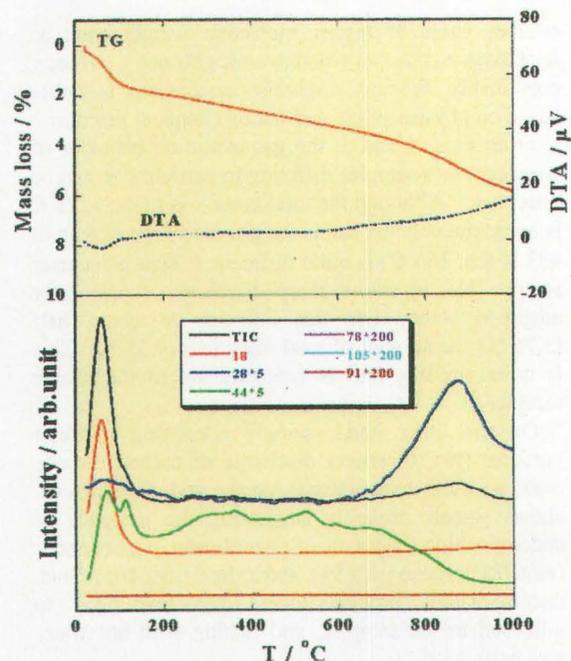


Fig.6 TG-MS curves of cedar-based woodceramics (4.0-1.7mm; No.8). The numerals in the figure stand for m/z.

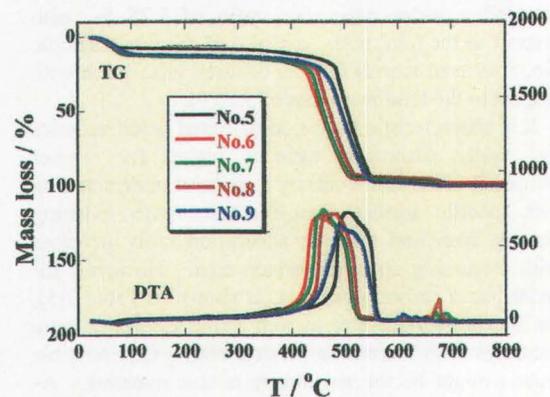


Fig. 7 TG-DTA curves of the samples in air.

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