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TG-DTA/GC-MS STUDY OF ODORLESS WOODCERAMICS FROM CHICKEN WASTES

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An odorless woodceramics (CH800), which was prepared by carbonizing chicken wastes with phenolic resin, was characterized by XRD and thermal analysis. CH800 was found to consist mainly of amorphous carbon (non-graphitizing carbon) as studied by XRD. Differing from carbonized chicken waste, CH800 was completely free of unfavorable smell. The source of strong smell of carbonized chicken waste was studied by using TG-DTA combined with EGA technique using gas chromatography and mass spectrometry (TG-DTA/GC-MS). As a result, it was found that CH800 was completely free of compounds having strong smell, i.e., ethanol, acetonitrile, pyridine, styrene, benzonitrile and benzofuran, whereas carbonized chicken waste contained all of these compounds.

Keywords: *adsorption, chicken waste, ecomaterial, micropores, smell, sorbent, TG-DTA/GC-MS, woodceramics*

Introduction

Woodceramics are, in a sense, carbon/carbon hybrid materials consisting of plant-originated amorphous carbon reinforced by glassy carbon generated from resin. They are higher in strength than wood, but lighter and readily machinable as compared with ceramics [1]. They were originally prepared by carbonizing wood or woody materials impregnated with thermosetting resin, such as phenol resin, in a vacuum furnace [2]. Thus, their potential for use as electromagnetic shielding materials [3], lubricating materials [4, 5], and sensor materials [6] has been reported.

Recently, woodceramics are considered environment benign materials or so-called ecomaterials, because they can be produced from carbon-containing industrial wastes and take part as a member of a closed material recycle system, and their by-products, such as the decomposition products, can be recycled [7]. For instance, in the apple products industry in Aomori Prefecture, Japan, about 4250 t/year of apple juice extract residues, i.e., apple pomace, which corresponds to about 20% of the raw material, is being wasted. Thus, woodceramics were produced from apple pomace, and detailed studies have been made on the effect of sintering conditions as well as characterization of them, such as densities, structures, and thermooxidative properties for use as sorbents [8, 9].

Similarly, as Japanese enjoy more western dishes, more eggs and chicken meat are consumed, and traditional farms are increasing scale to bring up poultries and broilers, resulting in the production of larger amount of chicken wastes (feces). It is reported that such chicken wastes amounting to 8.1 million tons from poultry and 5 million tons from other chickens are being disposed annually. This is becoming a serious problem also in US because, not only it lacks proper means to dispose large amount of wastes, but also such animal manure causes environmental concerns such as polluting water [10] and delivering unfavorable odor that annoy people.

As a measure for coping with this problem, it had long been proposed to use chicken wastes as agricultural fertilizers, since chicken feces contain elements and compounds such as calcium, potassium, nitrogen, magnesium, and the like in addition to carbon. This proposal is ideal in that the wastes can be used in a closed cycle in the farm sites. However, the chicken wastes or carbonized products obtained therefrom were found to have strong unfavorable smell, which was found as a serious problem to be overcome.

Thus, woodceramics using chicken wastes free from odor was characterized by X-ray diffraction (XRD) and thermal analysis. The chemical composition of carbonized chicken waste and woodceramics made from chicken waste (CH800) was determined by X-ray fluorescence spectroscopy (SQX). The reason why they are odor-free was investigated by mainly using simultaneous thermogravimetry-differential thermal analysis (TG-DTA) coupled with evolved gas

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analysis using gas chromatography and mass spectrometry (GC-MS).

Experimental

Samples

Woodceramics using chicken wastes (referenced as 'CH800' hereinafter) was prepared in a similar manner as the woodceramics stated before [2]; i.e., by bone-drying 600 g of chicken wastes (containing 40 mass% water) at 100–110°C, and was mixed with 400 g BELLPEARL S890 (phenolic resin produced by Kanebo Ltd.), which product was molten at 300°C for 3 h. Thus, CH800 was obtained by sintering at 800°C. As comparative sample, carbonized chicken waste was prepared in the same manner as CH800, except for mixing with BELLPEARL S890.

The content of elements other than carbon was determined by Rigaku ZSX system (SQX; XRF semi-quantitative analysis), and is given in Table 1. In Fig. 1 is shown the field-effect scanning micrograph (Carl Zeiss, Co. Ltd.) of CH800.

Specific surface area (SSA)

Specific surface area of the sample was determined by mercury porosimetry (Poremaster, Quantachrome Instruments), and multipoint BET method using nitrogen gas as adsorbate (Autosorb 1, Quantachrome Instruments).

XRD identification

XRD analysis on the as-received samples and heated samples (in air) were made using SCINTAG X'TRA AA85516 (ThermoARL) X-ray diffractometer equipped with Peltier cooled Si solid detector. Monochromatized $CuK_{\alpha 1}$ (0.15054 nm) was used as the radiation. Diffraction patterns were collected at 45 kV–40 mA, at 0.01° step and count time of 0.500 s over a range of 1.00 to 90.00° (2θ), at a step scan rate of 1.20° min^{-1}.

Simultaneous DSC-TG (SDT)

Differential scanning calorimetry (DSC) was performed simultaneously with thermogravimetric (TG) analysis using a simultaneous differential scanning calorimeter-thermogravimetric analyzer SDT2960 TA Instruments on about 10 mg each of samples in the temperature range of from R.T. to 1273 K at a heating rate of 2 K min^{-1}. The measurements were carried out under air flow of 100 mL min^{-1} (airgas compressed air (breathing grade), Type I, Grade D, 21% O_2 certified).

Simultaneous TG-DTA/GC-MS

Simultaneous TG-DTA/GC-MS measurements were performed on 35 mg each of samples using a TG-DTA TG8120 (Rigaku Corporation) coupled with QP-5050A (Shimadzu Corporation) in the temperature range of from R.T. to 1000°C at a heating rate of 20 K min^{-1} under helium gas flow of 300 mL min^{-1}, while holding all of the connecting parts with MS at 553 K for direct mode measurements. For trapping mode measurements to identify the gas species, GC-MS measurement was performed on 5 mg samples. The gas evolved in the temperature range of 30–300°C was collected, and was injected to the column at 290°C. A regular pore column (0.25 mm diameter, 30 m, 1.0 μm) was used.

Results and discussion

Sample characteristics

Figure 1 is the FE-SEM micrograph of CH800, showing rugged or scaly surface attributed to the heterogeneous nature of chicken feces. The as-received chicken feces is high in water content and contains soil, feedstock residue, and the like. Accordingly, pretreatment such as milling or crushing, followed by drying, is necessary. The sample shows rugged or scaly surface characteristic to the original chicken waste, but does not suggest having high porosity.

Since micropores smaller than 2 nm in diameter cannot be measured by mercury porosimetry, the specific surface area (SSA) was determined as 1.48 m^2 g^{-1} (mean value; at a diameter of 0.377 μm). The SSA obtained by nitrogen gas adsorption method (at 77 K) and analyzed by multipoint BET method was 33.4 m^2 g^{-1}.

Elemental analysis for the samples (Table 1) shows that chicken wastes contain Ca, K, P, Mg, and other metals, and in general, CH800 generally con-

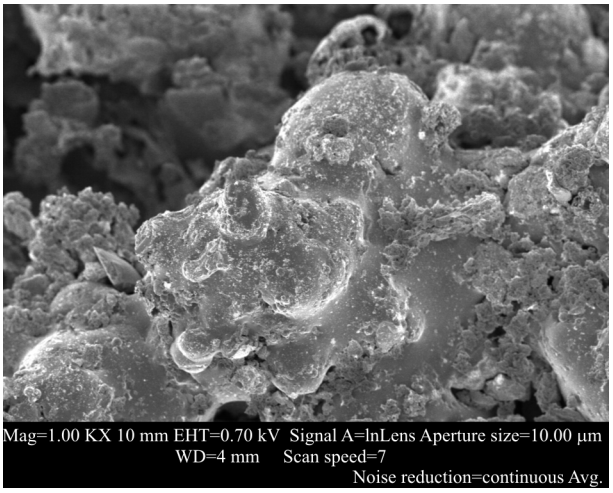

Fig. 1 FE-SEM photograph of CH800

Table 1 Composition of samples (SQX results in mass%)

Sample	Woodceramics	Comparative
	CH800 (granular)	carbonized chicken waste
O	25.7	22.8
Na	0.0	0.0
Mg	1.1	1.1
Al	0.2	0.3
Si	0.6	0.4
P	3.0	2.6
S	0.5	0.9
Cl	0.7	0.4
K	6.7	6.4
Ca	8.7	8.4
Cu	1.9	1.1
Zn	1.1	1.3
Total	50.2	45.7

tains, by mass, about 30% C, 10% Ca, 7% K, 3% P and 1% Mg. It is also known that chicken wastes also contain about 3–4% nitrogen.

Thermal change in air

Figure 2 shows the TG-DTA results for CH800 obtained in flowing air at a heating rate of 2 K min^{-1}. The mass loss occurs roughly in three steps; woodceramics typically contain about 5% of moisture, which is lost at temperatures below 210°C; about 60% is lost up to ca. 500°C in an exothermic reaction; and about 5% is lost between 500 and 600°C. Hence, the second mass loss is presumaly due to pyrolysis with overlapping combustion of volatile matter and pyrolysed products. The third mass loss is presumed attributed to the oxidative fragmentation of phenolic resin, which is discussed in detail hereinafter.

Figure 3 shows the XRD patterns for CH800 and for CH800 heated to 1000°C in air. From the XRD pattern, the original sample shows broad peak at 0.544 nm (2θ=15.90°). This is the so-called γ-band, which is believed to be derived from aliphatic chains [11]. It is known that this peak is not found in commercially available active carbon such as FLUKA05120. However, when heated to 1000°C in air, a sharp peak appears at ca. 0.344 nm, which is near to the *d*(002) spacing of glassy carbon (non-graphitizing carbon) or turbostratic structure [12]. Thus, this suggests that the original CH800 contain micro-graphite like structures having short-range ordering similar to active carbon fibers, which develop into graphene-like layers on heating [13].

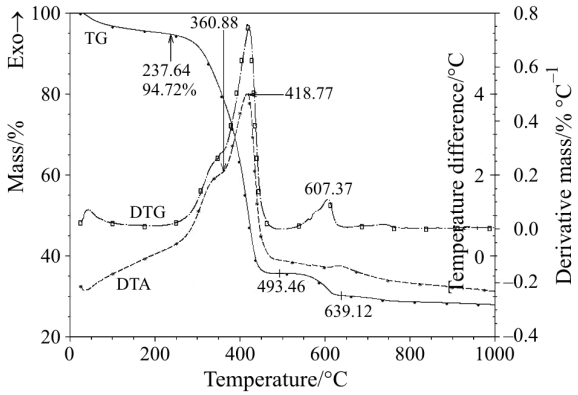

Fig. 2 TG-DTA curve of CH800 obtained in flowing air at a heating rate of 2 K min^{-1}

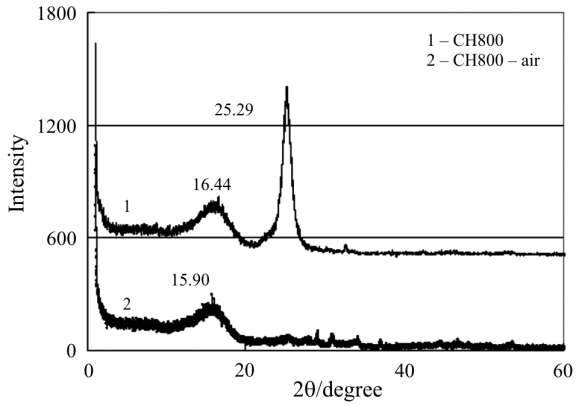

Fig. 3 XRD patterns for CH800 and for CH800 heated to 1000°C in air

Conclusively, in air, woodceramics prepared from chicken waste (CH800) is presumed to proceed as follows:

- to 210°C: desorption of water and other adsorbed gases
- 210–500°C: oxidative devolatilization to form amorphous carbon and cross-linking reaction (release of hydrocarbon fragments and combustion) and
- 500°C: fragmentation of aromatic polymers and oxidation, and decomposition of calcium carbonate contained as an impurity; the final mass% of about 30% is the residue obtained as oxides

TG-DTA/GC-MS study

Figures 4 and 5 each show TG-MS curves of chicken waste carbonized at 800°C and of CH800, respectively. DTA was used only for confirmation that the change occurs in an inert atmosphere. Figure 6 shows the MS-GC data for the same samples. The carbonized sample heated in inert gas (He) flow shows mass loss of about 5% up to 210°C mainly attributed to loss of H_2O and CO_2 or acetaldehyde (*m*/*z* 44) as was the case of heating in air, whereas the

mass loss of CH800 amounting to 10% is attributed to the desorption of water.

Referring to carbonized chicken waste shown in Fig. 4, the mass loss occurs in four steps; (1) at temperatures lower than 210°C (about 5% loss), (2) 210–400°C (about 2% loss), (3) 400–600°C (about 5% loss), and (4) 600°C– (about 13% loss). Differing from the case of CH800, the mass loss in (2) is mainly attributed to the species with *m*/*z* 44, which may be assigned to CO_2. Furthermore, the amount of mass loss in (3) is higher than the case of CH800, and shows evolution of species with *m*/*z* 128 (naphthalene) in two steps and with *m*/*z* 18 (H_2O). This may indicate dehydrogenation and recombination of hydrogen with dissociated fragments to form H_2O. In temperature region (3), fragments with *m*/*z* 152 (presumably biphenylene or acenaphthylene) and *m*/*z* 78 (benzene or pyridine) are found first (also yielding peak at *m*/*z* 91), followed by fragments with *m*/*z* 168 (dibenzofuran) and *m*/*z* 103 (benzonitrile). These fragments having benzene rings synchronously yield a signal at *m*/*z* 51. Thus, it can be seen that the reaction occurring in this temperature range with slight mass loss is attributed to fragmentation and the cross-linking reaction of phenolic resin. In particular, in the temperature range (4), it can be clearly understood that the mass loss at temperatures higher than 800°C is attributed to the evolution of species with *m*/*z* 28 (probably as C_2H_4, CO, molecular nitrogen), which shows progressive formation of graphene-like structure while releasing CO and C_2H_4.

Referring to the case of CH800 shown in Fig. 5, in the temperature range of 210–600°C, the total mass loss for CH800 in inert gas atmosphere is about 2%, and this is attributed to pyrolytic reaction of the phenolic resin; it is known that decomposition of the original phenolic structure proceeds and fractions of the phenolic resin is dissocated [14, 15]. Thus, *m*/*z* 128 and *m*/*z* 78 probably indicate presence of naphthalene and benzene, respectively, which accompany fragments with *m*/*z* 51 (which is frequently observed for molecules having benzene rings as stated above). The signal for *m*/*z* 168 increases intensity from 300°C, which may be assigned to the dissociation of dibenzofuran. In the temperature range of 600–700°C, the mass loss is about 5%. This mass loss accompanies evolution of species with *m*/*z* 44 (e.g., C_3H_8, CO_2), which is then followed by *m*/*z* 28. This mass loss is typical for phenolic resin in due course of forming graphene-like polycyclic structure at temperatures higher than 600°C [14, 15], in which fragments with or without heteroatoms are found to dissociate (probably as C_2H_4, CO, molecular nitrogen). Furthermore, the decomposition of impurities such as calcium carbonate

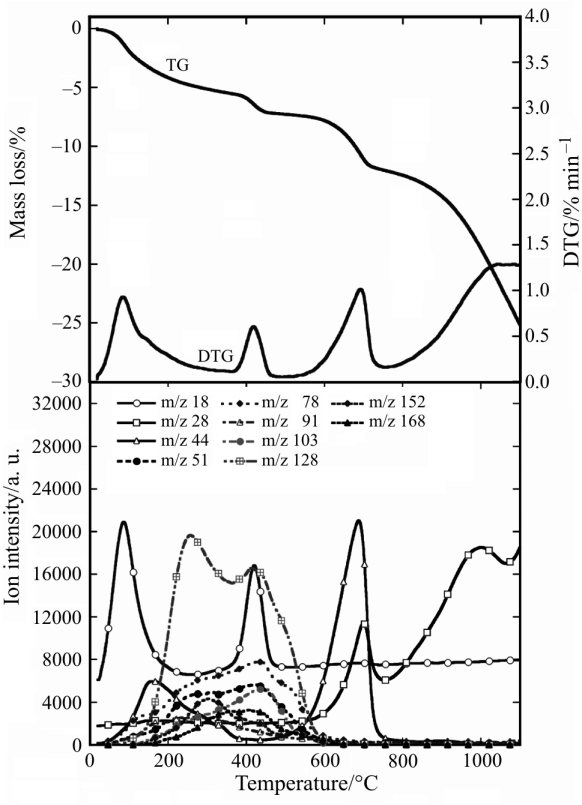

Fig. 4 TG-MS results in flowing helium for chicken waste carbonized at 800°C

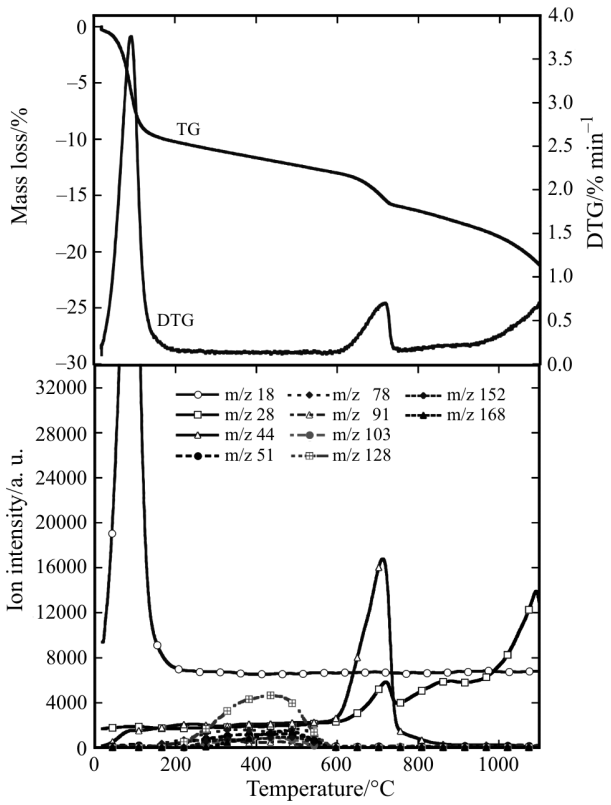

Fig. 5 TG-MS results in flowing helium for CH800 (woodceramics of chicken waste obtained at 800°C)

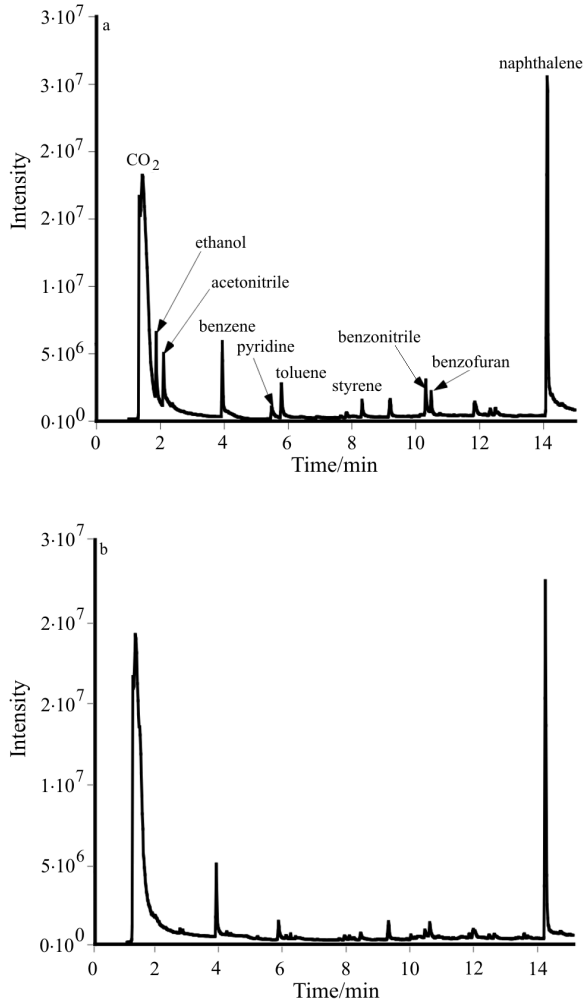

Fig. 6 MS-GC results showing source of strong smell of a – carbonized sample as compared with b – chicken waste woodceramics, CH800

may account for the release of carbon dioxide in the temperature range of 600°C or higher.

In Fig. 6 are shown the GC-MS results of the species obtained by trapping the gas evolved in the temperature range of 30 to 300°C. By comparing the results obtained on carbonized chicken waste (upper) with those of CH800 (lower), it can be understood that carbonized chicken waste evolves considerable amount of ethanol, acetonitrile, pyridine, styrene, benzonitrile, and benzofuran. These compounds all have strong odor.

Conclusions

A new environmentally benign material, i.e., odorless woodceramics (CH800), which was prepared by carbonizing chicken wastes with phenolic resin, was characterized by XRD and thermal analysis. It has been found that CH800 mainly consists of amorphous carbon as observed by XRD, but when heated to 1000°C in air, a sharp peak appeared at a *d*-spacing of ca. 0.344 nm, which is near to the *d*(002) spacing of glassy carbon (non-graphitizing carbon). This suggests that the original CH800 contains micro-graphite like structures having short-range ordering similar to active carbon fibers, which develop into graphene-like layers on heating.

CH800 differed from carbonized chicken waste in that it is completely free of unfavorable smell. The source of strong smell of carbonized chicken waste was studied by TG-DTA combined with EGA technique using mass spectrometry (TG-DTA/GC-MS). As a result, it has been found that carbonized chicken waste evolves compounds such as ethanol, acetonitrile, pyridine, styrene, benzonitrile, and benzofuran, but that CH800 was completely free of such compounds having strong smell.

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