Transactions of the Materials Research Society of Japan 29[5] 2435-2438 (2004)

Characterization of woodceramics derived from olive pomace

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As a new ecomaterial, hard Woodceramics were prepared successfully from olive pomace (wastes) by sintering olive pomace with phenolic resin at 1073K. Unlike to other woodceramics produced from cellulosic materials, the product showed characteristics similar to charcoal, showing development of graphite-like layers. This is presumably due to the presence of oil in the waste, which was confirmed by XRD and thermal analysis. However, woodceramics produced from olive pomace is thermally more stable than a simple charcoal, can be obtained in shaped structures, and, requires no activation treatment.

Key words: Woodceramics, TG-DTA/MS, EGA, olive pomace, ecomaterial, active carbon

1. 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 may use 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].

In the apple products industry in Aomori Prefecture, Japan, about 4250 t/year of apple pomace, which corresponds to about 20 % of the raw material, is being wasted (average taken for year 1997 to 2001). From ecological point of view, accordingly, studies on extracting wood vinegar, or on recycling of them as active carbon, friction materials, heater sheets, and Woodceramics, have been made [8] on apple pomace. Furthermore, detailed studies on the effect of sintering conditions of these apple-based Woodceramics and characterization on them, such as densities, structures, and thermoxidative properties for use as sorbents have been made[9,10].

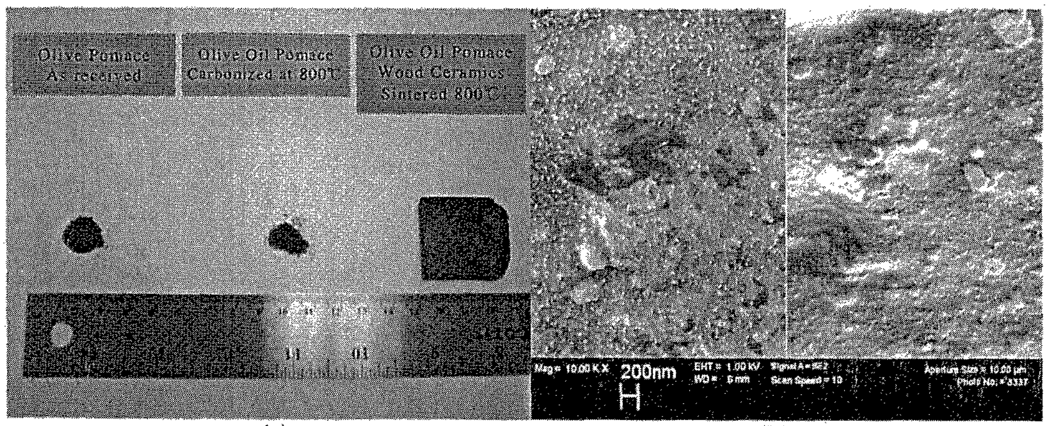
Similarly, the olive oil production is characterized by relevant amounts of by-products, namely solid residues, constituted by olive stones (seeds) and olive pomace, and liquid residues. In the Mediterranean area, where more than 95% of the world's olives are harvested, up to 30 million tons of residues arise per year[11]. At present, the residues are used as fuel because they yield a fairly high heating value, in the range of 14-18 MJ/kg. Super active carbons having a specific surface area of ca. 2000 m^2g^{-1} have been prepared from olive stones[12,13], but they require additional activation treatment.

Accordingly, an attempt of producing Woodceramics has been made to fully recycle the residues with an aim to obtain value-added products.. The present paper reports on the characterization of Woodceramics produced from olive pomace and olive stones by mainly using XRD and simultaneous thermogravimetry differential thermal analysis (TG-DTA) coupled with evolved gas analysis using mass spectrometry (MS).

2. EXPERIMENTAL

2.1 *Samples*

Woodceramics using olive pomace (OWC800) was prepared by impregnating olive pomace with 55 mass% phenolic resin PX-1600 (Honen Corporation), shaped, and sintered at 1073K. Figure 1 shows the outer appearance (a) and the field-effect scanning micrograph (b) of OWC800. They show porous surface characteristic to Woodceramics, but the topographic image as shown on the right hand side of Figure 1(b) suggests formation of a rather smooth surface as compared with MDF based woodceramics. As a reference material, carbonized olive pomace (OC800)



(a) (b)

Fig. 1 (a) Olive pomace, carbonized olive pomace, and OWC800; and (b) SEM photograph of OWC800; right hand side image show topographic image.

was also prepared by sintering at 1073K. Typical chemical composition of olive pomace is given in Table 1.

2.2 *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 Cu Kα1 (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 sec over a range of 1.00 to 90.00 deg (2θ), at a step scan rate of 1.20 deg min^{-1}.

2.3 *Simultaneous DSC-TG(SDT) Measurement*

Differential scanning calorimetry (DSC) was performed simultaneously with thermogravimetric (TG) analysis using a Simultaneous Differential scanning calorimeter-Thermogravimetric analyzer SDT 2960 (TA Instruments) of about 10 - 15 mg each of samples in the temperature range of from room temperature to 1273 K at a heating rate of 2 $Kmin^{-1}$. 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).

2.4 *Simultaneous TG-DTA/(GC)-MS*

Simultaneous TG-DTA/MS measurements were performed on about 15 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 1273 K at a heating rate of 20 $Kmin^{-1}$ under helium gas flow of 300 $mlmin^{-1}$, while holding all of the connecting parts with MS at 553 K for direct mode measurements.

3. RESULTS AND DISCUSSION

3.1 *Sample characteristics*

Since olive waste contains about 80% water, it can be understood from Table 1 that sugars account for about 11 mass%, and fibers account for about 88 mass% of the solid waste. Thus, it is suitable for producing Woodceramics similar to the case of woodceramics made from medium density fiber boards[4]. Thus, it can be tailored into a hard board as shown in Fig. 1. The board shows a smooth surface with luster.

Figure 2 shows the XRD pattern for OWC800. The sharp peak at 25.29° corresponds to so-called (002) diffraction with interlayer spacing of 0.352 nm, indicating the development of graphene-like layers[14]. The weak and broad peak at ca. 16° corresponds to a d-spacing of 0.550 nm, the so-called γ-band, which is believed to be derived from aliphatic chains[15].

Table 1 Composition of olive pomace

Components	
Soluble sugars (g/kg)	2.2
Glucose (ppm)	10.9
Saccharose (ppm)	18.7
Mannitol (ppm)	425.0
Nitrogen (g/kg)	13.4
Polyphenols (g/kg)	0.6
Total fiber (g/kg)	186.4
Ash (g/kg)	10.3

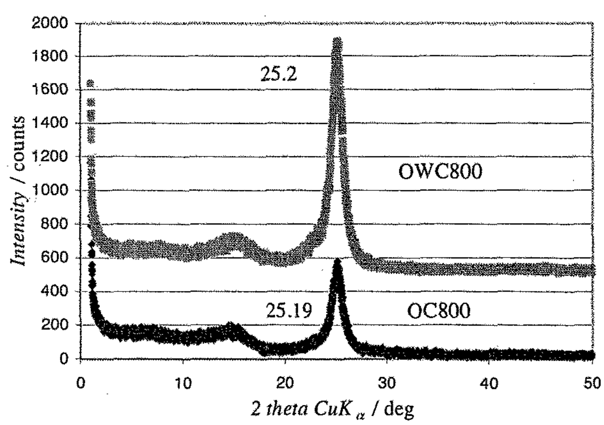


Fig. 2 XRD pattern of OWC800 and OC800.

However, the pattern for OWC800 resembles to that of OC800, only that the intensity for OC800 is relatively weak than that of OWC800. This result is different from the sugar-based Woodceramics obtained from apple pomace[10] in which no sharp peaks for graphene-like layers were observed. That is, since olive pomace contains oil, the aromatic chains derived from the original sample can develop layered structure similar to the lamella structure for soft carbon. The XRD pattern is similar to a standard charcoal, Fluka05120, which is presented elsewhere [16]. Thus, it can be presumed that OWC800 shows characteristics similar to charcoal.

Figure 3 shows the SDT curves for OWC800 obtained in air flow. The total mass loss is about 87.5 mass%, and this is in conformity with the ash content which accounts for about 12.5 mass% of the total solid waste. Large mass loss accompanying large amount of heat release occurs at ca. 523K to 673K, due to ignition and combustion of aromatic components similar to coal devolatilization in which pyrolysis and oxidation take place at the same time. The temperature range for this devolatilization is lower than that of commercially available charcoal (Fluka05120) by about 100 deg. The small mass loss at higher temperatures (873-1023K) is presumably due to the combustion of char generated during the precedent mass loss.

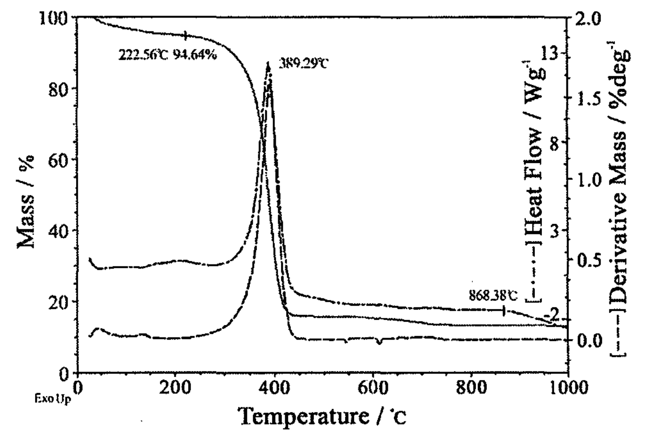


Fig. 3 TG(DTG)-DSC of OWC800 in air flow.

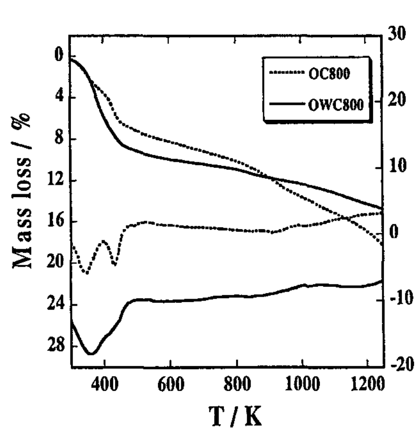


Fig. 4 TG-DTA curves of OWC800 and OC800 obtained in He gas flow.

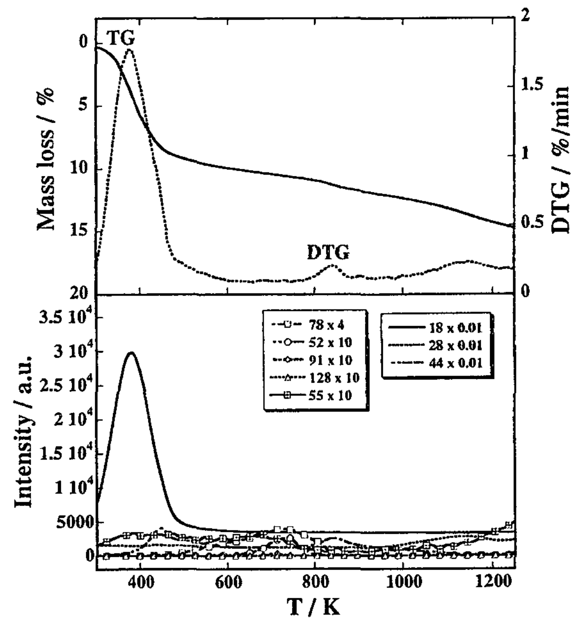


Fig. 5 TG(-DTG)/MS results for OWC800.

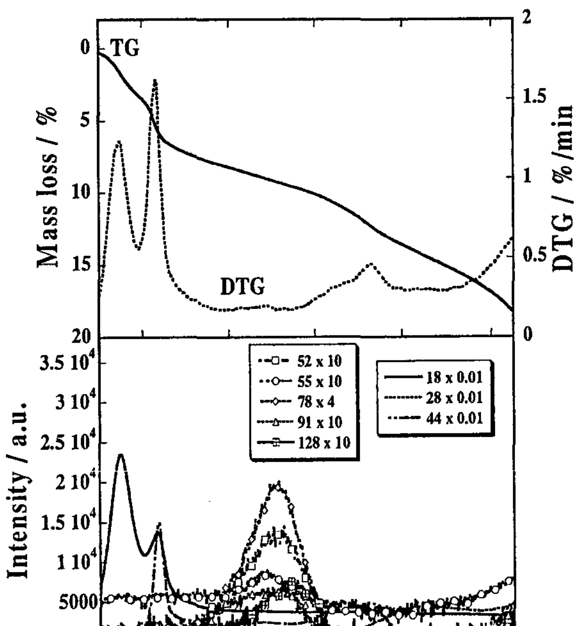


Fig. 6 TG(-DTG)/MS results for OC800.

3.2 *TG-DTA/MS results*

Figure 4 shows TG-DTA curves of OC800 and OWC800 obtained in He gas flow. Figures 5 and 6 show the TG(-DTG)/MS results for OWC800 and OC800, respectively. The carbonized sample OC800 heated in inert gas (He) shows two-step mass loss up to 473K mainly attributed to loss of adsorbed H_2O and CO_2 (m/z18 and m/z44, respectively). However, the mass loss for OWC800 is one-step, and is attributed to the loss of adsorbed moisture. Although the mass loss to ca. 800K is larger for OWC800, it can be seen that the mechanism therefor is simple. Furthermore, OWC800 is thermally more stable than OC800, since pyrolysis barely takes place under an inert gas atmosphere. More specifically, for OC800, evolution of gas species of aromatic fragments, such as benzene (m/z78, m/z52), toluene (m/z91), naphthalene (m/z128), and other aromatic fragments are observed to 873K, and a considerable amount of CO_2 is discharged at 773-873K. Furthermore, in OC800, a peak in DTG in the temperature range of ca. 873-1000K is mainly attributed to the discharge of CO (m/z28), and this shows that further carbonization takes place on the sample. This tendency is similar to other Woodceramics based on cellulosic materials[17]; however, olive pomace charcoals and olive pomace Woodceramics are similar to each other in XRD. This might be due to the fact that olive pomace contain oil residues that are more graphitizable as compared with cellulosic materials, and therefore graphite-like layers are easily developed in OWC800.

CONCLUSIONS

Hard Woodceramics were prepared successfully from olive pomace (wastes) by sintering olive pomace with phenolic resin at 1073K. Unlike to other woodceramics produced from cellulosic materials, the product showed characteristics similar to charcoal, showing development of graphite-like layers. This is presumably due to the presence of oil in the waste, which was confirmed by XRD and thermal analysis. However, woodceramics produced from olive pomace is thermally more stable than a simple charcoal, can be obtained in shaped structures, and, requires no activation treatment. However, additional study is necessary for applications such as adsorbents, abrasives, grinding media, or shaped bodies.

ACKNOWLEDGEMENTS

The authors thank Mr. S. Tachibana of Carl Zeiss, Co. Ltd., Kakuhiro Co. Ltd., and Mr. Yoshinaga of Kanebo, Ltd. The authors are also grateful to Prof. Ryoichi Yamamoto of the University of Tokyo and to Prof. Wei-Ping Pan of Western Kentucky University.

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(Received October 11, 2003; Accepted December 11, 2003)