Editor's Choice

doi:10.1246/cl.2010.998

A Novel Method to Discriminate between Plant- and Petroleum-derived Plastics by Stable Carbon Isotope Analysis

Yaeko Suzuki,*[1,2] Fumikazu Akamatsu,[1,2] Rumiko Nakashita,[1,3] and Takashi Korenaga[1]
[1]*Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0387*
[2]*Water Environment Research Group, Public Works Research Institute, 1-6 Minami Hara, Tsukuba, Ibaraki 305-8516*
[3]*Analytical Group, Japan Certification Service, 4-5-17 Chigasaki-higashi, Tsuzuki-ku, Yokohama, Kanagawa 224-0033*

(Received June 30, 2010; CL-100598; E-mail: ysuzuki@pure-foods.co.jp)

We determined stable carbon isotopic compositions ($\delta^{13}C$) of plastics to discriminate between plant- and petroleum-derived plastics. The $\delta^{13}C$ values of plastics derived from C_4 plants are significantly higher than those of petroleum-derived plastics. These results suggest that the stable isotope analysis would be useful in discrimination of plant-derived plastics from petroleum-derived plastics.

Petrochemical plastics have been extensively used in packaging of products like food, pharmaceuticals, cosmetics, and chemicals. The incineration of the plastic wastes always produces a large quantity of carbon dioxide and creates global warming. Moreover, it sometimes produces toxic gases such as hydrogen chloride, which contributes to the global pollution. Therefore, consumers demand packaging materials that are more natural, and recyclable.[1,2]

Due to increasing environmental concerns, interest in plant-derived plastics is growing significantly.[3] They are composed of renewable materials, such as starch from corn, sugarcane, beets, wheat, rice, and potatoes. Plant-derived plastic has low environmental impact, depending on the way it is produced.[1,4] Thus, plant-derived plastics can also contribute to CO_2-emission reductions. In addition, it does not leave toxic residue. Thus, numerous manufacturers are beginning to use or develop plant-derived plastics.

Poly(lactic acid) (PLA) is a biodegradable polyester, made from primarily of renewable agricultural resources (such as corn and sugarcane) following fermentation of starch and condensation of lactic acid.[1–4] At present, a number of shopping bags and containers could be made from PLA. Also, polyethylene (PE) has been made from sugarcane ethanol. A remarkable advantage of the sugarcane-derived PE is completely the same characteristics as traditional petroleum-derived PE, implying that it can be used in the existing processing equipment and recycling systems.

So far, plant-derived content of chemical products was determined by using conventional radiocarbon (^{14}C) analysis in accordance with procedures specified in ASTM D 6866-05.[5] It has been proposed that the modern carbon sources (i.e., plant or animal materials) have much ^{14}C while fossil carbon (i.e., petroleum) has substantially no ^{14}C. Thus, ^{14}C analysis has been employed as a reliable and valuable tool for verifying plant-derived content of chemical products including plastics.[6,7] However, it requires a very large amount of time consumption because of numerous analytical procedures. A simple analytical method, which rapidly finds plant-derived plastics, is necessary to resolve these problems.

Stable isotope analysis has widely been used to trace the origin of organic materials in various fields, such as ecology, biochemistry, and food authenticity.[8–10] The stable carbon isotopic composition ($\delta^{13}C$) of plant materials strongly depends on carbon fixation process such as the C_3 or C_4 cycle.[11] Most plants, including beets, wheat, rice, and potatoes, utilize the C_3 photosynthetic pathway to assimilate CO_2. The $\delta^{13}C$ values of these C_3 plants generally range from $-28‰$ to $-23‰$.[11] Corn and sugarcane are representatives of C_4 plants, in which the $\delta^{13}C$ values are generally around $-12‰$ to $-10‰$.[11] On the other hand, Yeh and Epstein et al. (1981) reported that $\delta^{13}C$ values of crude oil range from $-32.5‰$ to $-23.3‰$.[12] Thus, products derived from C_4 plants show higher ^{13}C content than those from C_3 plants and petroleum. These characteristics of $\delta^{13}C$ have been used for identification of industrial products such as sugars and alcohol.[13,14]

Therefore, in this study, we evaluate the applicability of stable carbon isotope analysis to discriminate between plant- and petroleum-derived plastics. The recent spread of elemental analyzer/isotope ratio mass spectrometry (EA/IRMS) facilitates a rapid and routine analysis of the isotopic composition of organic materials. This technique will be important for securing reliability of plant-derived products and for subsequently decreasing of CO_2 gas releases from petroleum incineration.

We collected raw materials; unprocessed corn ($n = 3$), sugarcane ($n = 3$), wheat ($n = 3$), rice ($n = 3$), and potato samples ($n = 3$) from feedstock. These samples (5–10 g) were dried and ground to a fine powder before the stable isotope analysis. PLA polymer from corn (C_4 plant, $n = 2$) was corrected. Plastics (PLA and PE) were also collected from PLA from rice (C_3 plant, $n = 4$) and corn (C_4 plant, $n = 12$), and PE from sugarcane (C_4 plant, $n = 3$), and petroleum ($n = 13$). These samples were weighted about 0.5 mg into a tin capsule (5 × 9 mm). The carbon stable isotopic composition was determined by EA/IRMS using a Delta V Advantage (Thermo Fisher Scientific, Bremen, Germany) interfaced with a FlashEA 1112 HT (Thermo Fisher Scientific, Bremen, Germany). The samples were combusted and reduced at 900 °C in a reactor filled with chromium(III) oxide, silvered cobaltous oxide, and copper wire under 70 mL min^{-1} of He flow rate. The produced gases were then passed through $Mg(ClO_4)_2$ to remove water. Finally, CO_2 gas was purified by gas chromatography with a molecular sieve 5 Å column at 40 °C, and the isotopic composition was determined by IRMS. The isotopic composition was reported in the δ notation:

$$\delta^{13}\mathrm{C}\ (‰) = [(^{13}\mathrm{C}/^{12}\mathrm{C}_{\mathrm{sample}})/(^{13}\mathrm{C}/^{12}\mathrm{C}_{\mathrm{PDB}}) - 1] \times 1000 \quad (1)$$

with PeeDee Belemnite (PDB) as the standard. The analytical precision (1σ) was within 0.1‰.

The $\delta^{13}C$ values were tested statistically by two-way analysis of variance (ANOVA) in the setting source (C_3 and

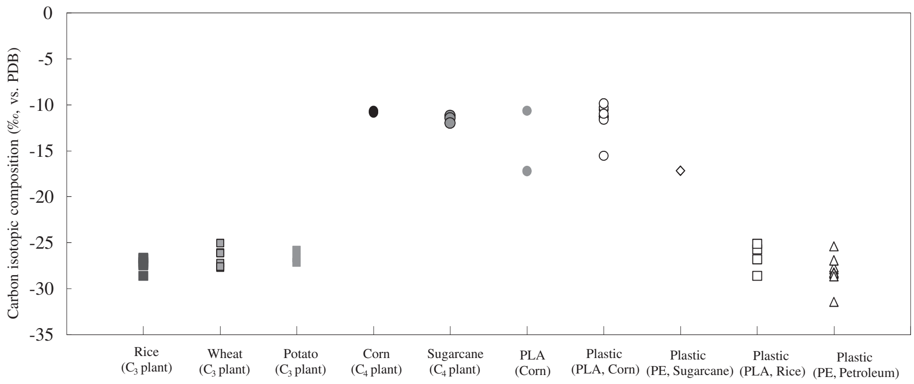

Figure 1. The carbon isotopic compositions of C_3 (rice, potato, and wheat) and C_4 (corn and sugarcane) plants and plastics derived from plants and petroleum.

C_4 plants and petroleum) and material types (raw and plastic) as fixed factors. When the interaction terms in the ANOVA were significant, multiple comparisons were made after one-way ANOVA, using Fisher's protected least significant difference (PLSD) test. For all tests, the α value of 0.05 was used to indicate statistical significance. All analyses were conducted using SPSS16.0 (SPSS Inc., Tokyo, Japan).

The δ^{13}C values of raw materials range from −27.5‰ to −26.6‰ for rice, −27.2‰ to −25.8‰ for potato, −27.7‰ to −27.6‰ for wheat, −10.8‰ to −10.7‰ for corn, and −15.1‰ to −12.1‰ for sugarcane (Figure 1). The δ^{13}C values of crude oil range from −32.5‰ to −23.3‰.[12] The ANOVA show a significant difference in the δ^{13}C among C_3 plants, C_4 plants and petroleum ($F_{2,43} = 311.82$, $P < 0.001$). Multiple comparisons (Fisher's PLSD test) show that the δ^{13}C values of C_4 plants are significantly higher than those of C_3 plants ($P < 0.001$) and petroleum ($P < 0.001$). But there is no significant difference in the δ^{13}C values between C_3 plants and petroleum ($P = 0.301$). These results are consistent with different photosynthesis pathway and resulting different δ^{13}C signatures between C_3 and C_4 plants.[11]

The δ^{13}C values of PLA polymer range from −17.2‰ to −10.7‰ (Figure 1). The δ^{13}C values of the plastics range from −17.3‰ to −10.0‰ for corn-derived plastics (PLA), from −28.6‰ to −25.8‰ for sugarcane-derived plastics (PE), from −28.6‰ to −25.8‰ for rice-derived plastics (PLA), and from −32.1‰ to −25.4‰ for petroleum-derived plastics (PE). There is no significant difference in δ^{13}C between plastics and raw materials ($F_{1,43} = 0.30$, $P = 0.587$). These results suggest the δ^{13}C of plastics directly reflects those of raw material. Moreover, δ^{13}C values of corn-derived PLA and sugarcane-derived PE were significantly higher than those of petroleum-derived plastics. These results suggest that the δ^{13}C values of plant-derived plastics reflect the botanical origin, and plastics derived from C_4 plants have significantly higher δ^{13}C values than products from petroleum. On the other hand, the δ^{13}C values of rice-derived plastics do not significantly differ from those of petroleum-derived plastics. Thus the carbon isotope analysis would be a useful method to differentiate between the C_4 plant- and petroleum-derived plastics.

This study clearly demonstrates that carbon isotopic composition can discriminate C_4 plant-derived plastics from petroleum-derived plastics (Figure 1). Moreover, unlike the traditional ^{14}C method, the analytical time of the EA/IRMS method (about 10 min per sample) facilitates the investigation of a large number of samples. Therefore, we strongly suggest that stable carbon isotope analysis will be employed as a new potential method to identify the C_4 plant-derived plastics, and that this method will contribute significantly for decreasing of CO_2 gas released from petroleum incineration and ultimately of global warming.

We are grateful to Mr. Joji Kanemichi, and Mr. Yoneshi Saito, for collecting the known origin samples and kindly providing the suggestions of plant-derived plastics.

References

1 M. A. Del Nobile, A. Conte, G. G. Buonocore, A. L. Incoronato, A. Massaro, O. Panza, *J. Food Eng.* **2009**, *93*, 1.
2 D. S. Cha, M. S. Chinnan, *Crit. Rev. Food Sci. Nutr.* **2004**, *44*, 223.
3 R. Auras, B. Harte, S. Selke, *Macromol. Biosci.* **2004**, *4*, 835.
4 T. Jin, H. Zhang, *J. Food Sci.* **2008**, *73*, M127.
5 ASTM International, Method D 6866-05: *ASTM International*, West Conshohocken, PA, **2005**.
6 G. A. Norton, S. L. Devlin, *Bioresour. Technol.* **2006**, *97*, 2084.
7 G. A. Norton, D. G. Hood, S. L. Devlin, *Bioresour. Technol.* **2007**, *98*, 1052.
8 E. Wada, *Jpn. J. Ecol.* **1997**, *47*, 333.
9 Y. Chikaraishi, Y. Suzuki, H. Naraoka, *Phytochemistry* **2004**, *65*, 2293.
10 S. Kelly, K. Heaton, J. Hoogewerff, *Trends Food Sci. Technol.* **2005**, *16*, 555.
11 B. N. Smith, S. Epstein, *Plant Physiol.* **1971**, *47*, 380.
12 H. W. Yeh, S. Epstein, *Geochim. Cosmochim. Acta* **1981**, *45*, 753.
13 J. Bricout, J. C. Fontes, *Ann. Fals. Exp. Chim.* **1974**, *716*, 211.
14 K. Ishida-Fujii, S. Goto, R. Uemura, K. Yamada, M. Sato, N. Yoshida, *Biosci. Biotechnol. Biochem.* **2005**, *69*, 2193.