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Anaerobic biodegradation tests of poly(lactic acid) and polycaprolactone using new evaluation system for methane fermentation in anaerobic sludge

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ABSTRACT

The anaerobic biodegradation tests of polycaprolactone (PCL) and poly(lactic acid) (PLA) powders were done at thermophilic temperature (55 °C) under aquatic conditions (total solid concentrations of the used sludge were 1.73% (undiluted sludge) and 0.86% (diluted sludge)) using a newly developed evaluation system. With this system, the evolved biogas is collected in a gas sampling bag at atmospheric pressure. This method is more convenient than using a pressure transducer or inverted graduated cylinder submerged in water. The biodegradation of PCL powder (10 g, 125–250 μm) in the diluted sludge stopped in about 47 days when the biodegradability reached 92%. The biodegradability of PLA powder (10 g, 125–250 μm) in undiluted sludge was 91% at about 75 days. The biodegradability of PLA powder (10 g, 125–250 μm) in diluted sludge was 79% at about 100 days. The biodegradability of PLA powder (5 g, 125–250 μm) in diluted sludge was 80% at about 85 days. It was found that the PCL and PLA powders were quite degraded using the new evaluation method. In addition, the smaller particle size PCL powder was biodegraded faster.

1. Introduction

Biodegradable plastics have been developed over the past 30 years. These bioplastics are expected to be used as food packaging materials or agricultural materials which became waste along with organic waste such as food waste or the remaining parts of vegetables. These plastic wastes with organic waste can be added to or used as feedstock for biological recycling and recovery in an aerobic composting plant or anaerobic biogasification plant. The aerobic biodegradation behavior of plastics has been well studied and the degrading microorganisms have been isolated and identified [1–5]. The evaluation of the anaerobic biodegradation of plastics, however, is still in development and some investigations have been reported [6–11]. Anaerobic fermentation has some advantages compared with aerobic fermentation such as composting. The anaerobic fermentation plant is nearly a closed system then the less stenchful aerobic one with a shorter processing time, and produces CH_4 as an energy source. The anaerobic degradation of organic substances occurs in several steps, and the organic substances are finally degraded to CO_2 and CH_4. The amount of CO_2 and CH_4 from organic substances in anaerobic fermentation is expected by Buswell equation [12] as follows:

$$C_nH_aO_b + (n - a/4 - b/2)H_2O \rightarrow (n/2 + a/8 - b/4)CH_4 + (n/2 - a/8 + b/4)CO_2 \quad (1)$$

The produced CH_4 is expected to be recovered as energy. In a typical anaerobic fermentation plant, the feedstock is not completely degraded to CO_2 and CH_4 during the real retention time of a continuously operated fermentation tank to obtain an economical treatment, then the remaining nondegraded materials are used as a liquid fertilizer or compost.

Some of the biodegradable plastics, such as polycaprolactone (PCL) and poly(lactic acid) (PLA), were not easily degraded in mesophilic temperature (33–37 °C) in anaerobic fermentation [6,9,11]. The thermophilic (about 55 °C) anaerobic fermentation plants using garbage slurry or cow manure as a feedstock, in which total solid concentration is about 10%, are build and operated in Japan recently. In these plants, the non-biodegradable garbage collecting bags were separated from feedstocks of anaerobic fermentation. The product made with biodegradable plastics and its waste is thought to be anaerobically degraded with household organic waste or animal manure in thermophilic anaerobic fermentation plant. The fish box, which is used for fish packing and carried in a market, made of a poly(lactic acid)-based polymer foam was anaerobically degraded with vegetable debris in a Kyoto fish market under thermophilic conditions in the Kyoto Project (2003). In this project, the PLA-based polymer foam was hydrolyzed into pieces at around 10 days and completely degraded within 30–40 days at 55 °C.

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To make sure plastics are fit for biological recycling, their biodegradability must be measured in a laboratory, preferably by standard test methods. Two International Standard (ISO) methods and several American Society for Testing and Materials (ASTM) methods were published as the international standard test methods in evaluating anaerobic biodegradation (ISO 14853, 15985, ASTM D5210, D5526, etc.). Table 1 lists the test conditions of these methods. There is no test method for aquatic and slurry conditions (total solid concentration (TS) below 20%) at a thermophilic temperature (about 55 °C) in the present test methods. ISO 14853 and ASTM D5210 (equivalent to ISO 14853) are aquatic biodegradation tests (TS 0.1–0.3% or >0.1%) at a mesophilic temperature (about 35 °C) in a synthetic growth medium with a mixed microbial population derived from a compost or wastewater treatment facility. In these tests, the sludge was diluted with a mineral salts medium, so only bacteria utilizing the polymer as a carbon source in the mineral salts medium grew. The microbial population is thought not to reflect the original sludge. Typical biodegradable plastics, such as polycaprolactone (PCL) and poly(lactic acid) (PLA), have shown a slight biodegradability when using these methods. ISO 15985 and ASTM D5526 are tests using over a 20% TS concentration (a high-solid condition) sludge at a thermophilic temperature (about 52 °C in ISO 15985) or mesophilic temperature (about 35 °C in ASTM D5526) with mixed inoculums derived from anaerobic digesters operating only on pretreated household waste. In a high-solid sludge, it seemed that the procedure to make the sludge have over a 20% solid concentration and then homogeneously transferring the high-solids sludge to the vessel and stirring of high-solids sludge is not easy. The biogas amount from the vessel without a sample (only sludge) is used as the base amount of the sludge in each sample vessel. A high amount of biogas from the blank vessel is assumed to be due to the high remaining organic concentration in the high-solids sludge.

The Japan BioPlastics Association (JBPA) and Japan Bioindustry Association (JBA) started the standardization project with the National Institute of Advanced Industrial Science and Technology (AIST), Fuji-Tokoha University, and the University of Shizuoka for anaerobic degradation test methods of bioplastics in recognition that a new convenient anaerobic biodegradation test method is necessary to estimate the biodegradation and biorecycling of the generally using bioplastic polymers, such as PCL and PLA. The use of the original sludge in a commercially operated anaerobic fermentation tank is more suitable for evaluating the biodegradability in this tank because of the simulated real conditions. However, the sludge is diluted with a medium or concentrated for the present test methods. To evaluate the degradability of bioplastics in the original sludge concentration, we tried to biodegrade plastics at the thermophilic temperature (55 °C) under aquatic conditions. Thus, we used a newly developed evaluation system (commercial name "MODA-B" developed by Yahata-Bussan Co., Ltd., Japan) for the test of anaerobic biodegradation. In this apparatus, the gas evolved from the experimental vessel is collected in a gas sampling bag, then the gas volume is measured by a syringe, and the biogas component is analyzed by gas chromatograph (GC). This method is more convenient to measure the evolved biogas volume than using a pressure transducer or inverted graduated cylinder submerged in water.

In this paper, we report the results of the anaerobic biodegradation of generally using bioplastics, such as PCL and PLA, using the MODA-B apparatus at a thermophilic temperature (55 °C) under aquatic conditions in which the TS is 0.8–1.8% in the anaerobic sludge, to confirm the optimal evaluation conditions for complete anaerobic biodegradation of bioplastics.

2. Experimental section

2.1. Plastic sample

Cellulose powder of thin-layer chromatography grade with a particle size of less than 20 μm (Cellulose microcrystalline, Merck, Germany) and PCL (Mw 65,000, Aldrich, USA) were purchased. PLA (H-400, Mitsui Chemical. Co., Ltd., Japan) was kindly supplied from Mitsui Chemicals (Japan). The PCL and PLA powders were prepared by previously described methods [13,14]. Three different particle size powders less than 125 μm (Av. 75.5 μm), between 125 μm and 250 μm (Av. 180.7 μm), and between 250 μm and 500 μm (Av. 297.6 μm) were used on the basis of ISO/DIS 10210.

2.2. Apparatus for anaerobic biodegradation test

The MODA-B apparatus (Yahata-Bussan Co., Ltd., Japan) is shown in Fig. 1. The sludge and test material are sealed in the test vessel (1.5 L) and incubated at 55 °C. The sludge (1.4 L) is stirred by exhausting the gas phase from the upper headspace to the bottom of the vessel using a gas pump, then mixing by gas bubble lifting. A panel sheet heater attached to the outside vessel with a surrounding cloth envelope maintained the temperature and control of the vessel temperature used a thermostat sensor in the middle of the vessel. The evolved biogas is collected in a gas sampling bag, which is an aluminum laminate with a four-layer structure (volume 2–5 L) and Teflon cock. The biogas volume in the bag was measured using a glass syringe (500 mL).

2.3. Procedure of anaerobic degradation test

There is no anaerobic fermentation plant operating at 55 °C around our laboratory, therefore we made the sludge adapted at 55 °C. To make the sludge adapted at 55 °C, the sludge from the tank operating at around 37 °C was preincubated at 55 °C. The anaerobic sludge as indicated in Table 2 was divided from Yamada

Table 1
Anaerobic biodegradation evaluation methods based on International Standards.

	ISO14853	ISO15985	ASTM D5210	ASTM D5526
Total solid concentration	0.1–0.3%	>20%	>0.1%	35, 45, 60%
Incubation temperature	35 ± 2 °C	52 ± 2 °C	35 ± 2 °C	35 ± 2 °C
Volume	0.1–1 L	>750 mL	100 mL	>800 g
pH	6.8–7.2	7.5–8.5		7.5–8.5
Sample amount	20–200 mg/L (as organic carbon)	20 g/vessel	Sufficient carbon content sample	Sufficient carbon content sample
Inoculum	Domestic sewage or laboratory-grown anaerobic sludge	Household waste	Well-operated anaerobic sludge	Household waste

ISO14853: Plastics – determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system – method by measurement of biogas production.
ISO15985: Plastics – determination of the ultimate anaerobic biodegradation and disintegration under high-solids anaerobic-digestion conditions – method by analysis of released biogas.
ASTM D5210: Standard test method for determining the anaerobic biodegradation of plastic materials in the presence of municipal sewage sludge.
ASTM D5526: Standard test method for determining anaerobic biodegradation of plastic material under accelerated landfill conditions.