Biodegradation of poly-ε-caprolactone and its unexpected effects in an attempt to reduce ammonia emission during composting

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Abstract

Ammonia is the greatest nuisance odor component among the exhaust gases that evolve during the composting process. The present study examined the effect on ammonia emission reduction resulting from the addition of poly-ε-caprolactone (PCL), a biodegradable plastic, into composting raw material. After approximately three days from the start of composting, a clear difference was observed in the concentration of CO₂ and the cumulative emission of carbon between composting with and without the addition of PCL. This difference indicated that the PCL began to decompose to CO₂ on approximately the 3rd day of composting. The percentage of PCL decomposition finally reached to approximately 46% on the 7th day of composting. The concentration of NH₃ in the composting with PCL was half or smaller than that observed in the composting without PCL on the 3rd day of composting. Moreover, the concentration of NH₃ became extremely low after 4th day of composting with PCL. These results clearly demonstrated not only that PCL is compostable, but also that it is capable of suppressing NH₃ emission during the process of composting. In addition, it was shown that biodegradable plastics other than the PCL reduced ammonia emissions during the composting process as well, although the magnitude of the reduction differed according to the type of biodegradable plastic.

1 Introduction

The management of solid waste is a growing concern in many countries. Municipal solid waste is a major component of the total solid waste generated by society, and the composting of municipal solid waste is one of the most useful methods of treating organic waste and reclaiming it for use on farm land. Such practice has
gained some attention, although composting treatment of municipal solid waste is not yet widespread in Japan. One reason for this is that compost products contain significant quantities of impurities, including plastic, which can not be accepted by farmers. Due to the present circumstances, many kinds of biodegradable plastic materials have recently been developed; these types of materials can be degraded along with organic wastes during composting [1].

Another reason for the lack of popularity of composting is the odor generated by the composting process; this odor is a so-called complex odor, i.e., a mixture of many different kinds of compounds [2-6]. Among these, NH₃ is the greatest nuisance, in particular when raw materials that contain high concentrations of nitrogen are used. For quite some time, methods for reducing or eliminating the odor generated by the composting process have been studied and tested. Recently, special attention has been paid to biofilter technology, which uses microorganisms and is considered to be economical [3,5]. In addition to studies researching methods of deodorizing the composting process, other studies have focused on how odor is generated by the conditions present upon composting [2,4,7,8]. It is expected that through such studies, a composting process that generates a minimum of odorous compounds will be found.

In the present study, we demonstrate the unexpected additional advantage of ammonia odor reduction by addition of biodegradable plastic among composting material. To our knowledge, no previous studies have described this effect resulting from the addition of biodegradable plastic on the reduction of NH₃ emission during the composting process.

2 Materials and methods

2.1 Biodegradable plastic

The biodegradable plastic used in this study consisted of fine particles of poly-e-caprolactone (PCL) with the trade name PLACCEL H7 (Daicel Chemical Industries, Ltd., Tokyo). The molecular weight of the PCL was ca. 70,000 and the diameter of the PCL particles ranged from 63 to 250 μm.

2.2 Raw materials for composting

A commercial dog food with the trade name VITA-ONE soft™ (Japan Pet Food Co. Ltd., Tokyo) was used as a model of organic waste in place of real organic fractions in municipal solid waste. In the preliminary experiments, the dog food gave good reproducible composting data, provided its composition was uniform [9]. The carbon and nitrogen contents of the dry weight basis of the dog food, as determined by elemental analysis, were 46.0 and 5.3 percent, respectively. Thus, the carbon:nitrogen ratio was 8.7:1. The dog food was minced and then mixed with sawdust (as a bulking agent) and inoculum with the trade name Alles G™ (Matsumoto laboratory of microorganisms Co. Ltd., Matsumoto, Japan). PCL particles were added to create a ratio of 10:9:1:10 among dog food, sawdust, inoculum, and the PCL on a dry weight basis. Thus the ratio of PCL to the composting mixture was 33%. A blank experimental composting run was carried out without the addition of PCL. At the start of both experiments, the pH level was adjusted to 8.5 by the addition of slaked lime, and the moisture content was adjusted to 60% by the addition of dis-
tilled water.

2.3 Composting operation

Figure 1 depicts a schematic diagram of the experimental system. A mini-reactor was used that consisted of a cylinder (45 mm in diameter, 100 mm in depth) made of Pyrex glass and was equipped at the top and bottom with silicone rubber stoppers and glass pipes for aeration. The air was first introduced into a flask containing NaOH solution for eliminating CO$_2$, then was passed through a bubbler prior to reaching the reactor in order to saturate the air with moisture. The aeration rate was maintained at 0.135 L/h throughout the experiment. It was ascertained in the preliminary experiment that the aeration rate was sufficient for maintaining aerobic conditions. The raw composting mixture with and without PCL were placed into the reactor at a weight of 13 and 10.86 wet-g, respectively, and the reactor itself was placed in an incubator (Model LTI-1000, EYELA Co., Ltd., Tokyo) in order to regulate the temperature. The temperature was raised from room temperature to a set point of 50 °C at a constant rate of 2 °C/h, and the temperature of 50 °C was then maintained until the 7th day, when the composting operation was stopped.

The exhaust gas from the composting reactor was introduced into a 5 L-plastic bag made of polyvinyl fluoride (Tedlar Bag™, Omi Odaïr Service Co. Ltd., Omihachiman, Japan) for 12 h, and the plastic bag was changed twice daily at 12-h intervals. The volume of exhaust gas captured in the plastic bag was measured, and the concentration of CO$_2$ and NH$_3$ were analyzed with Kitagawa gas detector tubes (Komyo Rikagaku Kogyo K.K., Tokyo). The quantity of CO$_2$ evolved during each 12 h period was determined by the CO$_2$ concentration and exhaust gas volume measured, and the cumulative CO$_2$ that had evolved up to a certain composting time was calculated. The cumulative emission of carbon ($E_C$) corresponding to the degree of decomposition of organic matter was defined as the molar ratio of carbon lost as CO$_2$ to the carbon contained in the dog food alone. Thus the $E_C$ value could
potentially be larger than 100%, if the biodegradable plastic was decomposed. The cumulative emission of nitrogen ($E_N$) was also calculated as the molar ratio of nitrogen lost, i.e., the relationship between nitrogen in the raw material, not including the PCL (the PCL contains no nitrogen), and the emitted $NH_3$.

The composting material was mixed with a sterilized spatula within the reactor every 24 h. A total of eight reactors were used for each composting run in order to measure changes in pH and chemical substances over time. The composting for these reactors was initiated at the same time and the composting process in subsequent reactors was interrupted at each turning and at the end of the composting period. Then, the compost sample from each reactor was subjected to pH and chemical analyses.

2.4 Chemical analyses

Two types of chemical analyses were carried out; one analysis measured the enzymatic activity of the PCL degradation, and the other analysis measured the molecular weight distribution of the PCL degradation intermediates. In order to determine the enzymatic activity of the PCL hydrolysis, i.e., PCL degradation, lipase activity was measured. The compost sample withdrawn from the reactor was first mixed with sterile water, and was then homogenized. The homogenate was centrifuged and filtrated with a 0.45 μm pore-sized membrane filter in order to prepare the extract for measurement. The lipase activity was determined by the Lipase kit S assay system (Wako Pure Chemical Industry, Ltd., Tokyo). Since lipase hydrolyzes lipids, oils, and fats in addition to the PCL in the composting material, the lipase activity contributing to the PCL hydrolysis was determined by the difference between lipase activities in two composting samples, namely one with and one without the addition of PCL.

The molecular weight distribution of the degradation intermediates of the PCL remaining in the compost was measured by gel permeation chromatography (GPC). One wet-g of compost withdrawn from the reactor was suspended in 3mL of THF (tetrahydrofuran) and the extract was filtrated with a 0.45 μm-pore membrane filter for preparation of a GPC liquid sample. The GPC analyzer (Model LC-10A series, Shimadzu Corporation, Tokyo), equipped with an RI detector and a Shodex K806L column (Showa Denko K.K., Tokyo), was operated at a 40 °C column temperature and a THF elution rate of 0.8 mL/min.

3 Results and discussion

3.1 The course of PCL decomposition during composting

The time course of the CO$_2$ concentration and of the cumulative emission of carbon for the composting with and without PCL, as well as the percentage of PCL decomposition, are shown in Fig. 2. A clear difference was observed in the concentration of CO$_2$ and cumulative emission of carbon between composting with and without PCL after about 72 h from the start of the composting period. The percentage of decomposed PCL was determined from the difference between the quantity of CO$_2$ evolution in the presence of PCL and that in the absence thereof [10]. In addition, the percentage of decomposed PCL began to elevate about 72 h after the initiation
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Figure 2: Time course of the concentration of CO$_2$ ($C_{CO2}$) and cumulative emission of carbon ($E_c$) for composting with PCL (closed symbols) and without PCL (open symbols), and the percentage of PCL decomposition ($X_{PCL}$).

of the composting period; this result corresponded to a substantial observed difference in the cumulative emission of carbon between the composting with and without PCL. In other words, when the PCL was added to the dog food, the organic matter contained in the dog food most likely decomposed first, followed by the decomposition of the PCL. The final value of the percentage of PCL decomposition attained was approximately 46%.

3.2 Effects of PCL on reduction of ammonia emission

The time courses of pH change, ammonia concentration, and cumulative emission of carbon for the composting with and without PCL are shown in Fig. 3. In the composting without PCL, the pH value dropped once during the early stages of composting (24 h), then the pH value rose again and leveled off at around pH 8.6. It
was assumed that the pH value decreased in the first stages of composting due to the accumulation of organic acids caused by the degradation of the dog food. Then, the pH value increased again due to both the production of ammonia associated with protein degradation in the dog food and to the decomposition of organic acids [10]. In contrast, the pH value in the compost sample with PCL decreased once initially, then rose to a value similar to that obtained in the compost sample without PCL. However, the pH value began to decline again starting at 72 h, reaching near 7.2 at the end of composting (a secondary decrease in pH). A secondary decrease in the pH value was not observed in the composting without PCL.

In the composting without PCL, the NH$_3$ began to evolve into exhaust gas at 36 h after the initiation of the composting period, then peaked at 72 h and continued to evolve until the end of the composting period, although the concentration of NH$_3$ gradually lowered with time. However, in the composting containing PCL, the concentration of NH$_3$ was half or smaller than that of the composting without PCL at the middle stage of composting, and the concentration of NH$_3$ was extremely low at the latter stages of composting. Furthermore, differences in the cumulative emission of

Figure 3: Time course of the pH value, the concentration of ammonia (C$_{NH_3}$), and the cumulative emission of nitrogen ($E_N$) for composting with PCL (closed symbols) and without PCL (open symbols).
nitrogen became apparent at the final stage of composting, a result which corresponds to the fact that a significant difference in the pH value between compost samples with and without PCL was observed at the latter stage as well. Therefore, it was determined that PCL degradation led both to a decrease in the pH value of the composting material and to the reduction of NH\textsubscript{3} emission into the exhaust gas. These results may suggest that the ammonia was neutralized by certain acidic intermediates from the degrading PCL and/or the ammonia was consumed by microorganisms for the production of microbial cell mass.

### 3.3 Enzymatic hydrolysis of PCL and PCL degradation intermediates

Figure 4 represents the course of lipase activity contributing to PCL hydrolysis that was determined by the difference between lipase activities observed in two compost samples, one with and one without PCL. The lipase activity began to increase after 72 h of composting, then rapidly increased with the progression of time, and finally leveled off at approximately 3.8 IU/g-dry solid composting material.

The time course of the GPC pattern in the composting with and without PCL are shown in Fig. 5. The GPC peaks observed when the molecular weight was lower than 1,000 were similar for both groups, i.e., those with and without PCL. It was thus determined that these peaks were derived from the raw material not including the PCL. A peak appeared near a molecular weight of 70,000 in the composting sample with PCL, which represented the original PCL added to the raw compost material. The peak height near 70,000 began to decrease gradually after 72 hours from the start of composting, indicating that the PCL began to degrade vigorously around this time. This result corresponded well to the increase in steepness of the PCL decomposition curve gradient (cf. Fig. 2). In addition, lipase activity increased rapidly after 72 hours of composting (cf. Fig. 4). Figure 5 demonstrates that the PCL degradation intermediates were not detected throughout the composting period with PCL, and that the concentrations of degradation intermediates in the compost

![Figure 4: Time course of lipase activity contributing to PCL degradation in the composting with PCL.](image)
Figure 5: Time course of the GPC pattern in the composting with and without PCL.

sample were extremely low, if they were at all present. These results suggest that immediately after they were produced, the PCL degradation intermediates were successively decomposed into lower molecular weight components that are easily consumed by microorganisms. Since the PCL degradation intermediates did not accumulate in the compost throughout the composting period, it can be concluded that the ammonia emissions were not reduced due to neutralization via PCL degradation. Therefore, it may furthermore be concluded that the suppression of ammonia gas emission by addition of PCL into the raw compost material was mainly due to the consumption of nitrogen by microbial cells. Further research will be required to clarify the detailed mechanisms of this process.

3.4 Effects of the other biodegradable plastics on the reduction of ammonia emission

Three other kinds of biodegradable plastics (i.e., condensation polymer of 1, 4-butandiol, succinic acid and adipic acid (PBSA: BIONOLLE #3001, Showa Denko K.K., Tokyo/Showa Highpolymer Co., Ltd., Tokyo), polymerized lactic acids (PIA: LACEA H-100PL, Mitsui Chemical Inc., Tokyo), and polymer alloy of poly-ε-caprolactone and other biodegradable plastics (CL: Daicel Chemical Industries, Ltd., Tokyo)) were used in the experiment to examine the effect of various kinds of biodegradable plastics on the reduction of ammonia emissions. The particle diameters of these plastics were adjusted to be similar to that of the PCL, i.e., within a range of 63 to 250 μm.

Fig. 6 shows the final values of the percentage of decomposition for each biodegradable plastic, and the cumulative emission of nitrogen when each biodegradable plastic was mixed in with the raw material and when biodegradable plastic was
The final values of the percentage of decomposition for each biodegradable plastic ($X_{BP}$) and the cumulative emission of nitrogen ($E_N$) when each biodegradable plastic was mixed with the raw material. Keys for the abscissa represent the types of biodegradable plastic used, and the control (CTRL) without the addition of a biodegradable plastic, eliminated from the raw material (the control experiment). The final value of the percentage of decomposition gradually decreased in the order PCL > PBSA > CL > PLA. The percentage of PCL decomposition was 46% and thereby the highest among all of the plastics, and that of PLA was 27.8%, i.e., the lowest among all of the plastics. The difference in the percentage of decomposition of these biodegradable plastics appeared to depend on the specific composition of the plastic. The final value of the cumulative emission of nitrogen gradually decreased, and thus the reduction of ammonia emission occurred in the order PCL > PBSA > CL > PLA; it should be noted that the difference in this reductive effect among PBSA, CL, and PLA was small. As a result, it was concluded that all of the biodegradable plastics used in the present study degraded well during the composting process and that they all suppressed the emission of ammonia to various extents. Moreover, the magnitude of the suppressive effect differed with the type of biodegradable plastic under consideration.

4 Conclusion

The results obtained in this study demonstrated clearly that PCL is compostable, and that it is also capable of suppressing NH$_3$ emissions during the composting process. Recently, many types of biodegradable plastics have been developed in order to address the issue of the disposal of plastic waste materials. It is expected that the use of biodegradable plastic will contribute to solving the odor problem associated with composting, and will also promote the practice of composting both organic waste and biodegradable plastic itself.
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