



## Material Behaviour

## Control of biodegradability of triple-mixed aliphatic polyester films with calcined calcium oxide fine powder



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## ABSTRACT

Biodegradable mulch films are important agricultural materials for environmental protection and labor savings. To investigate the effect of calcium oxide fine powder on the degradation behavior of triple-mixed aliphatic polyester, films were prepared by thermal kneading a triple-mixed plastic matrix with calcined calcium oxide fine powder derived from scallop shells, followed by an inflation method. Three kinds of commercial biodegradable aliphatic polyesters, poly(lactic acid), poly(butylene succinate-co-adipate), and poly(butylene succinate-co-lactate), were mixed to form the triple-mixed matrix. The resulting films and, for comparison, two types of commercial mulch films, poly(butylene succinate) and poly(butylene adipate-co-terephthalate), were investigated using hydrolysis and soil burial tests for 180 d. The biodegradability of these films was examined by observing the time evolution of film weight loss, total organic carbon content, pH of the medium, and surface morphology using scanning electron microscopy. Addition of calcium oxide fine powder as a modifier significantly accelerated the speed of film degradation, and as the amount of CaO added was increased, the film degradation rate as well as the ability to suppress the acidification produced by the organic acids increased. As a result, quick-acting composite films containing a large proportion of poly(butylene succinate-co-adipate) were successfully prepared in this study.

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## 1. Introduction

Agricultural mulch films are widely used because they can control soil temperature, prevent soil erosion, reduce water consumption, and suppress weeds. However, the common plastic films used today are non-biodegradable plastics, such as low-density polyethylene (and in some cases high-density polyethylene or linear low-density polyethylene), poly(vinyl chloride), polybutylene, or copolymers of ethylene with vinyl acetate [1]. These plastics must be removed from the fields after harvesting to prevent soil pollution and other environmental impacts. The use of biodegradable mulch films seems to be a promising solution to solve these problems, because they can be incorporated into the soil at the end of the crop season and ultimately decomposed to carbon dioxide and water by soil microorganisms in the field.

Among the various commercial biodegradable polymers, poly(lactic acid) (PLA) is one of the most important, the monomers of which are generally derived from renewable resources such as corn, sugar, and potatoes [2]. PLA is attractive for application in biomedical products, packaging, and clothing owing to its competitive cost, high strength and elastic modulus, transparency, and excellent biocompatibility [3]. However, the inherent brittleness of PLA is a major drawback that prevents its widespread application, especially as a mulch film. Many efforts have been made to improve the toughness of PLA. For example, PLA has been blended with other more flexible and biodegradable polymers such as poly(butylene adipate-co-terephthalate) (PBAT) [4], poly(ethylene glycol) (PEG) [5], and poly(hydroxybutyrate) (PHB) [6]. Plasticizers such as epoxidized palm oil [7], epoxidized soybean oil [8], oligomeric lactic acid [9], limonene [10], and natural rubber [11] have also been used to improve the mechanical properties of PLA.

In this study, PLA and poly(butylene succinate-co-adipate) (PBSA) were mixed to form a plastic matrix and prepare a film.

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However, composites prepared by simple blending still suffer from poor impact resistance because of the phase separation and poor interfacial adhesion between the two immiscible components [12]. Therefore, the compatibilizer poly(butylene succinate-co-lactate) (PBS-co-PLA), which has both succinate and lactate portions, was used to enhance the interaction between PBSA and PLA. Considering the brittleness of PLA, PBSA was used in large proportions in this study. Under composting conditions, the PLA film degraded within three weeks [13]. However, as an agricultural mulch film, after the harvest season, the partially degraded PLA should be plowed into the soil. The degradation rate of PLA films is relatively slow in the soil, so calcined calcium oxide fine powder derived from scallop shells was added to improve the degradation rate of PLA. As reported in our previous paper [14], calcium oxide was used not only to control the degradation rate of the mulch films but also to neutralize the organic acids generated during the hydrolysis of the biodegradable polymers.

## 2. Experimental

### 2.1. Materials

PLA which included 2–3 mol% of D-lactide content was purchased from Unitika Limited (Japan) [15]. Its commercial name is Terramac® TE2000, and its number average molecular weight ( $M_n$ ) is  $6.7 \times 10^4$  g/mol, glass transition temperature ( $T_g$ ) is 55 °C, and melting temperature ( $T_m$ ) is 159 °C. PBSA was supplied by Showa Denko K.K. (Japan). Its commercial name is Bionolle® 3001,  $M_n = 8.3 \times 10^4$  g/mol,  $T_g = -41$  °C, and  $T_m = 84$  °C. PBS-co-PLA (the ratio of PBS: PLA determined by  $^1\text{H}$  NMR = 94:6 mol%) was obtained from Mitsubishi Chemical (Japan). Its commercial name is GS Pla® AD92W,  $M_n = 3.7 \times 10^4$  g/mol,  $T_g = -45$  °C, and  $T_m = 81$  °C. All the molecular weights were measured at 45 °C by gel permeation chromatography (GPC) using two PS gel columns (Shodex KF-804-L and KF-803-L), Hitachi L-6000 pump, Hitachi D-2520 GPC integrator, and Shimadzu YRD-880 RI detector, with tetrahydrofuran as eluent at a flow rate of 1 mL/min. PS standards were used to calibrate the molecular weight.  $T_g$  and  $T_m$  were determined by differential scanning calorimetry (Bruker AXS DSC 3200S) at a heating rate of 10 °C/min under a nitrogen atmosphere. Calcined calcium oxide fine powder derived from scallop shells was supplied by Kohkin Kenkyujo Inc. (Japan) and was used as the modifier. It was heated in an electric furnace at 900 °C for 2 h before use to improve the purity (98.6%). Carbon black was supplied by Meisai Chemical Corporation.

Further, for comparison, two types of commercial biodegradable mulch films were investigated using hydrolysis and soil burial tests: poly(butylene succinate) (PBS) purchased from Tsujino Plastic Corporation (Japan) with the commercial name “Biomaruchi” and PBAT obtained from Sekisui Film Corporation (Japan) with the commercial name “Nodoka black”.

### 2.2. Film preparation

Three kinds of commercial biodegradable aliphatic polyesters, Terramac (PLA), Bionolle (PBSA), and GS Pla (PBS-co-PLA), were mixed in a weight ratio of 20:70:10, respectively, to form a triple-mixed matrix. Biodegradable composites were prepared by thermal kneading of the triple-mixed matrix with the calcined calcium oxide fine powder (2 and 5 per hundred resin, phr) and carbon black (1 phr). The compounding was achieved using a twin-screw extruder at 170 °C by Meisai Chemical Co., Ltd. (Japan). Then films with a thickness of 20  $\mu\text{m}$  were molded by an inflation method at 170 °C. This inflation molding was supported by SKY Film Co., Ltd. (Japan).

### 2.3. Biodegradability tests

#### 2.3.1. Hydrolysis test

To perform the hydrolysis test, films ( $6 \times 100$  mm) of each type of sample were placed into test tubes filled with 15 mL of deionized water. Next, each test tube was tightly closed, put into a water bath, and continuously shaken at 40 °C. The films were evaluated at 10, 20, 30, 60, 90, and 180 d. 18 test tubes were prepared for each type of sample, 3 of which were taken for further analysis at each hydrolysis time.

First, the films were removed from the test tubes and dried in a vacuum oven at 40 °C to remove moisture. Then, the weight of the films was recorded before and after testing. The weight loss of the film was then calculated as follows:

$$\text{Weight loss} = [(M_0 - M_1)/M_0] \times 100\%$$

where  $M_0$  and  $M_1$  are sample weights before and after the hydrolysis test, respectively. Then, the pH of the degradation medium was later measured using a glass-electrode-type hydrogen-ion concentration meter (GST-5731C, pH meter: HM-25R, DKK-TOA Co., Ltd). Finally, the total organic carbon content (TOC) of the degradation medium was analyzed using a TOC-V CPH/CPN (Shimadzu Co., Ltd).

#### 2.3.2. Soil burial test

To perform the soil burial test, films ( $20 \times 20$  mm) were buried in rich soil (approximately 20 g) in a wide-mouthed glass bottle (capacity 60 mL) at room temperature. The relative humidity was kept at approximately 45%, managed by a soil-moisture-measuring instrument (DM-18, Takemura Electric Works Co., Ltd.). The films were evaluated at 10, 20, 30, 60, 90, and 180 d. 18 glass bottles were prepared for each type of sample, 3 of which were taken for further analysis at each time.

On selected days of the soil burial test, the weight loss of the films was measured using the same method as that in hydrolysis test. The pH value of the soil was measured using a soil pH meter (HI99121N, Hanna Instruments Japan Co., Ltd.).

#### 2.3.3. Surface morphology observations

A scanning electron microscope (SEM; model JSM-5610LV, Japan Electronics Co.) was used to examine the surface deterioration of film samples after each period of exposure to soil. All samples were coated with a thin layer of gold and were subsequently examined under an acceleration voltage of 15 kV.

## 3. Results and discussion

### 3.1. Hydrolysis test

The results of film weight loss, TOC, and pH value of the medium after the hydrolysis test are shown in Fig. 1. As time passed, the weight of the films gradually decreased. As for the composite films containing CaO, the rate of weight loss increased dramatically within the first 10 days, and then became slower. The final weight loss of the composite films with 2 phr CaO [CaO(2)] and 5 phr CaO [CaO(5)] reached 12.4% and 19.6%, respectively. The degradation rate of the films was accelerated by increasing the amount of calcium oxide fine powder in the films. However, the weight loss of commercial mulch films without CaO, PBS, and PBAT was very small.

The TOC values of all films correlated with the weight loss rate and increased as time passed. Composite films with higher CaO content showed higher TOC values, which correspond to the weight loss results. As time increased, the pH of the media containing

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