

Biodegradable Polyurethane Materials from Bark and Starch. II. Coating Material for Controlled-Release Fertilizer

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ABSTRACT: Biodegradable polyurethane foams (PUFs) as coating materials for the controlled release of fertilizer were prepared from a four-component system consisting of diisocyanate, polyester, *Acacia mearnsi* bark, and corn starch. Ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ was used as a fertilizer to evaluate the effects of the preparation conditions on the release ratio. The release ratio of $(\text{NH}_4)_2\text{SO}_4$ decreased with an increasing amount of biomass in PUFs and increasing sizes of sample particles; the ratio increased with increasing

doses of water, which was used as a foaming agent in the preparation of polyurethane, regardless of the amount of coating material. The remaining fertilizer in the polyurethane seemed to be released completely because the PUFs were degradable, to some extent, by soil microorganisms. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2948–2952, 2002

Key words: polyurethanes; biodegradable; polyester

INTRODUCTION

The rational application of fertilizer is a very important subject that is directly associated with saving energy and protecting the environment, farmland, and crops. The controlled release of fertilizer is an effective method for applying fertilizer rationally and represents one of the major developments in the fertilizer industry.

Fertilizer coating, which is also called fertilizer packing, is a universal controlled-release method. Fertilizer is insulated from the soil by a coating material and dissolves into the soil slowly.¹

There are three major types of materials used for coating. The first includes inorganic materials, such as sulfur, silicate, and phosphate, as reported by the Tennessee Valley Authority in 1961. The second consists of thermosetting resins, such as urea–formaldehyde resin. The third includes thermoplastic resins, most of which are polyolefins and blended polyolefins. Of these resins, low-density polythene, polypropylene, ethylene/carbon monoxide copolymer, and poly(vinyl acetal) have been often used as coating materials for controlled release according to the demands of different fertilizers and soil conditions.² However, after the release of fertilizers, remaining coating materials in the soil are very difficult to degrade and can

accumulate over time to become a new type of white pollution. Therefore, a new kind of coating material has to be developed that is readily available, undergoes osmosis with water, and is environmentally safe and biodegradable.

Polyurethane foams (PUFs) have been widely used in the fields of fibers, foams, elastomers, and protective coatings. They can improve edaphic moisture and ventilation because of their multicell structures.³ The addition polymerization of diisocyanates (DIs) with polyols is the basic process in their synthesis. Natural polymers are expected to be used as polyols in the preparation of biodegradable polyurethane (PU). The introduction of plant components into PU formulations has been reported.⁴ Lignin, lignocellulose, and corn starch (CS) have been added to PUF formulations as replacements for synthetic polyols. PUFs derived from *Acacia mearnsi* bark (BK) have the ability to adsorb heavy metal ions and proteins because of the BK component.⁵ Recently, we found that wattle tannin and BK could be successfully incorporated into PUF formulations and that they enhanced the biodegradability of some wood-rotting fungi and soil microorganisms.⁶

In this study, we tried to use BK-PUFs and BK/CS-PUFs as coating materials for controlled release. The effects of the preparation conditions on the properties of the coating materials are discussed.

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EXPERIMENT

Materials

BK (80-mesh pass) purchased from Fujian and cornstarch (CS) purchased from Jiangsu were dried in an

oven at 105°C for 24 h before use. Adipic acid, poly(ethylene glycol) (PEG) 400, silicon oil, triethylenediamine (TEDA), dibutyltin dilaurate (DBTL), trimethylolpropane (TMP), diphenylmethane diisocyanate (MDI), ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, and other reagents were obtained commercially without any further purification.

Preparation of the polyester (PES)

Adipic acid (145 g), PEG 400 (320 g), trimethylolthane (10.9 g), and xylene (20 g) were mixed, and the mixture was heated to 250°C within 2 h and maintained at this temperature with stirring in a nitrogen atmosphere. The reaction was conducted until the amount of water distilled from the condensation reached 95% of the theoretical amount. The hydroxyl and carboxyl group contents in the PES were 1.65 and 0.12 mmol/g, respectively, which were determined according to Fang et al.⁷ The viscosity (2900 cP at 25°C) was measured with a Brookfield viscometer.

Preparation of the PUFs and packaging of $(\text{NH}_4)_2\text{SO}_4$

Definite amounts of BK and CS were dissolved in PES with stirring at 80°C for 5 h. After the solution cooled, a surfactant (Y_{10366} silicon oil), catalysts (TEDA and DBTL), a crosslinking agent (TMP), and a foaming agent (water) were added with stirring and were followed by the addition of MDI (MDI index = 1.0) with stirring at 2400 rpm for 15 s. $(\text{NH}_4)_2\text{SO}_4$ particles were added, and the mixture was stirred at 10 rpm for coating until the coating system was uniform. Then, it was put into an oven at 50°C to solidify.

Measurement of the release properties

The most important characteristic of a coating material is the release ratio. Samples of PUF-packed $(\text{NH}_4)_2\text{SO}_4$ were weighed and put in Buchner funnels with filler paper. Then, the samples were poured out and rinsed with 10 mL of distilled water as a simulation of rain in nature (once every 15 min). The filtrate containing $(\text{NH}_4)_2\text{SO}_4$ was collected, and the amount of $(\text{NH}_4)_2\text{SO}_4$ was titrated by the formaldehyde method.⁸ For comparison, $(\text{NH}_4)_2\text{SO}_4$ without packing was also tested under the same conditions.

The release ratio was calculated with the following equation:

$$\text{Release Ratio (\%)} = m_{s1}/m_0 \times 100$$

where m_0 is the primordial amount of $(\text{NH}_4)_2\text{SO}_4$ coated with PU and m_{s1} is the amount of $(\text{NH}_4)_2\text{SO}_4$ in the filtrate.

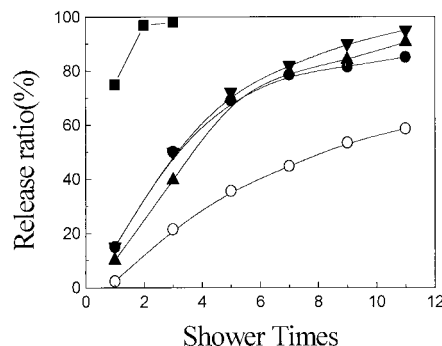


Figure 1 Effect of the amount of $(\text{NH}_4)_2\text{SO}_4$ coated with PU on the release ratio: (▼) 50 g packed with 20% BK in PU, (●) 30 g packed with 20% BK in PU, (▲) 10 g packed with 20% BK in PU, (○) 10 g packed with 10% BK and 10% CS in PU, and (■) 10 g without a coating. NCO/OH = 1.0; silicon oil (Y_{10366}) content = 2.0%; TEDA content = 0.02%; DBTL content = 0.25%; water content = 0.5%; $(\text{NH}_4)_2\text{SO}_4$ size = 1–3 mm.

Assay of biodegradability with indoor soil burial

The assay method of indoor soil burial was employed to evaluate the biodegradability of PU containing 0% BK (with 20% TMP), 10% BK, 20% BK, 30% BK, and 15% BK and 15% CS. The soil was obtained from the test forest of Fudan University, was sifted for the removal of hardened clumps, plant debris, and other sundries, and was placed into plastic boxes (40 cm × 25 cm × 15 cm) with holes in the covers. The PU blocks (20 mm × 20 mm × 20 mm) were buried in a certain array at a depth of 10 cm. The soil was kept moist with deionized water and placed in a room at ambient humidity (37–92%) and temperature (20–35°C). Three blocks were taken from each group for the measurement of their weights after drying at 60°C every month. The weight loss was calculated from the difference in the weights before and after the incubation of each block.

Scanning electron microscopy (SEM) photographs of PUFs were obtained with a Hitachi S-520 scanning electron microscope. Fourier transform infrared (FTIR) spectra were obtained from KBr pellets of BK-PU and BK/CS-PU with an FTIR spectrometer (Nicolet Magna IR-550).

RESULTS AND DISCUSSION

Effect of $(\text{NH}_4)_2\text{SO}_4$ coated with PU

To reduce product cost, we hoped to use less coating material to pack more fertilizer. Different amounts of $(\text{NH}_4)_2\text{SO}_4$ were added to a PU liquid containing 20% BK so that samples with different coating thicknesses would be obtained. The release ratios of $(\text{NH}_4)_2\text{SO}_4$ are shown in Figure 1. The release ratio of $(\text{NH}_4)_2\text{SO}_4$ coated with BK-PU was controlled and showed similar results, regardless of the amount of $(\text{NH}_4)_2\text{SO}_4$. In fact, different amounts of $(\text{NH}_4)_2\text{SO}_4$ packaged with

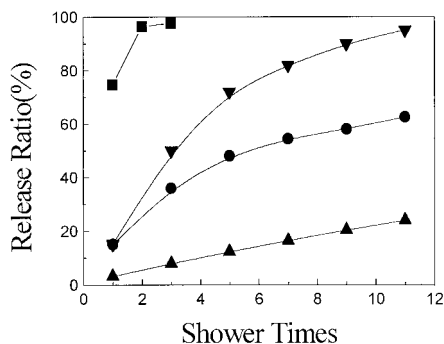


Figure 2 Effect of the $(\text{NH}_4)_2\text{SO}_4$ particle size on the release ratio: (∇) 1–3 mm, (\bullet) 4–6 mm, (\blacktriangle) 7–9 mm, and (\blacksquare) 1–3 mm without a coating. NCO/OH = 1.0; silicon oil (Y_{10366}) content = 2.0%; TEDA content = 0.02%; DBTL content = 0.25%; water content = 0.5%; BK content in PU = 20%.

the same amounts of PU indicated differences in the coating layer thickness. Therefore, the coating layer thickness was not important, so we could reduce the coating cost with a coating mechanism. When CS was used to replace 10% BK in PU, the release ratio decreased. However, the release ratio of $(\text{NH}_4)_2\text{SO}_4$ without a coating increased. Therefore, the PU coating layer effectively restricted water contact with $(\text{NH}_4)_2\text{SO}_4$.

There are two common methods of controlled release.² First, $(\text{NH}_4)_2\text{SO}_4$ is brought into direct contact with water and dissolved in the water; it is then taken away with flowing water, and this is called the *dissolve process*. Second, $(\text{NH}_4)_2\text{SO}_4$ permeates through a coating material via the concentration difference between the two sides of the coating layer, and this is called the *permeation process*. In this study, carbon dioxide, which was generated from the reaction of MDI with water used as a foaming agent and with silicon oil (Y_{10366}) used as an open cell surfactant, produced large amounts of open cells in PU. Therefore, this release process was mostly the dissolve process.

The release ratio was more effectively controlled when PU was prepared by the addition of CS partly replacing BK (15% BK and 15% CS). This result suggested that the CS component could reduce the opening of cells in the PU structure. Therefore, high-encumbrance PU could be obtained by the addition of CS to the PU formulation.

Effect of the $(\text{NH}_4)_2\text{SO}_4$ particle size on the release ratio

Samples with different particle sizes were used in release tests to evaluate the effects of the fertilizer particle size on the release ratio, as shown in Figure 2. The release ratio increased with decreasing particle size. It could be explained that samples with smaller sizes had larger surface areas and that water permeated into them more easily; this made their release ratios higher than those of large ones. However, the

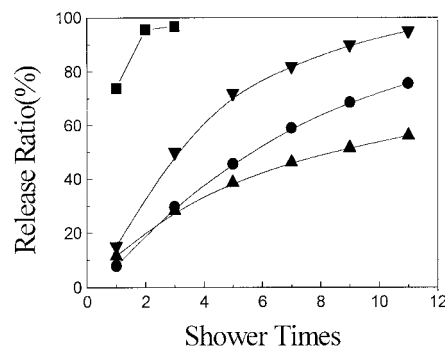


Figure 3 Effect of the water dosage in PU on the release ratio: (∇) 0.5% water in PU, (\bullet) 0.25% water in PU, (\blacktriangle) 0% water in PU, and (\blacksquare) 10 g of $(\text{NH}_4)_2\text{SO}_4$ without a coating. NCO/OH = 1.0; silicon oil (Y_{10366}) content = 2.0%; TEDA content = 0.02%; DBTL content = 0.25%; $(\text{NH}_4)_2\text{SO}_4$ size = 1–3 mm; BK content in PU = 20%.

coating cost may be increased when a fertilizer with smaller particles is packaged. Therefore, we should choose the proper particle sizes to satisfy the demands of different cases.

Effect of the water dosage used in the PU preparation

PUFs were prepared with different amounts of water for the evaluation of the effects of water on the release ratio (Fig. 3). Water reacted with isocyanate groups to produce carbon dioxide as a foaming agent. An increase in the water content increased the number of open cells in PUFs. Therefore, an increase in the water dosage in the PU formulation could improve the dissolve process for fertilizer release.

Effect of the BK content in PU

The release ratios of $(\text{NH}_4)_2\text{SO}_4$ coated with PU prepared with different amounts of BK are shown in

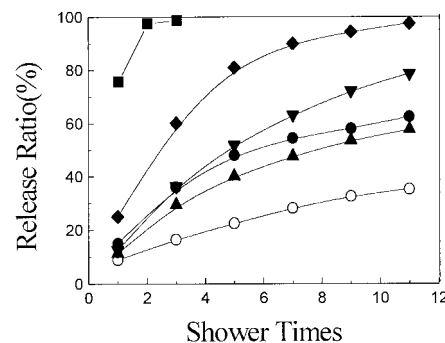


Figure 4 Effect of the biomass content on the release ratio: (\blacklozenge) 0% BK in PU (with 20% TMP), (∇) 10% BK in PU, (\bullet) 20% BK in PU, (\blacktriangle) 30% BK in PU, (\circ) 15% BK and 15% CS in PU, and (\blacksquare) 10 g of $(\text{NH}_4)_2\text{SO}_4$ without a coating. NCO/OH = 1.0; silicon oil (Y_{10366}) content = 2.0%; TEDA content = 0.02%; DBTL content = 0.25%; $(\text{NH}_4)_2\text{SO}_4$ size = 4–6 mm; water content = 0.5%.

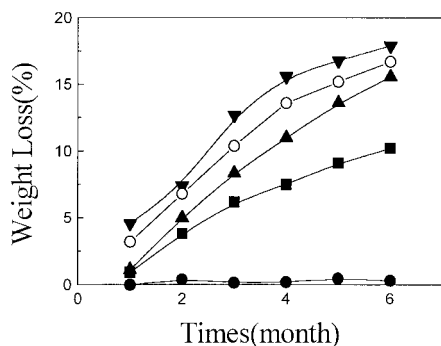


Figure 5 Effect of the soil microorganism treatment on the weight loss of PUFs: (●) 0% BK in PU (with 20% TMP), (■) 10% BK in PU, (▲) 20% BK in PU, (○) 30% BK in PU, and (▼) 15% BK and 15% CS in PU.

Figure 4. The release ratios decreased with increasing BK content in PU. The BK component acted as crosslinking points and hard segments in PUFs, as described in a previous article.⁶ Therefore, the increase in the amount of the crosslinking agent could result in difficulty with the release. However, the BK component seemed to adsorb fertilizer because BK-PU had good adsorption for proteins and some heavy metal ions, as reported in another article.⁵

When CS was used to replace BK partially (15% BK and 15% CS), the release became difficult. This result is similar to the findings shown in Figure 1 and suggests that the CS component might reduce the number of open cells in PU.

Biodegradation of the PU material

In general, at least 15–30% of a fertilizer packed in a coating material is difficult to release because of the decrease in the concentration difference between the inside and outside of the coating material. It was

thought that if a biodegradable coating material was used to pack fertilizer, the remaining fertilizer could be released completely in the last stage of release. Therefore, PUF blocks were buried in soil for an evaluation of the holistic, apparent, and interior variations through analyses of weight losses, SEM photographs, and hydrogen-bond changes.

Weight loss of PU

The weight losses of PU based on biomass increased with increasing periods of soil microorganism treatment, as shown in Figure 5. When CS partially replaced BK, the BK/CS-PU (15% BK and 15% CS) showed faster weight loss than those containing BK only. These results indicated that the CS component in PU decomposed more easily than the BK component. However, almost no change was observed in TMP-PU. Therefore, it is suggested that biomass contributes to PU biodegradation when biomass is introduced into the PU formulation.

SEM photographs of PU

SEM photographs of PU surface changes are shown in Figure 6. The representative structure of multicell PU (A) was expanded (B) and damaged (C) during the soil microorganism treatment. This phenomenon indicated that a PU coating material based on biomass could provide an additional release based on degradation in addition dissolve and permeation release. Therefore, it is suggested that PU can contribute to controlling not only the release in the initial release stage but also an additional release with coating material degradation in the last stage, so that the fertilizer could be released uniformly over the whole fertilizer period.

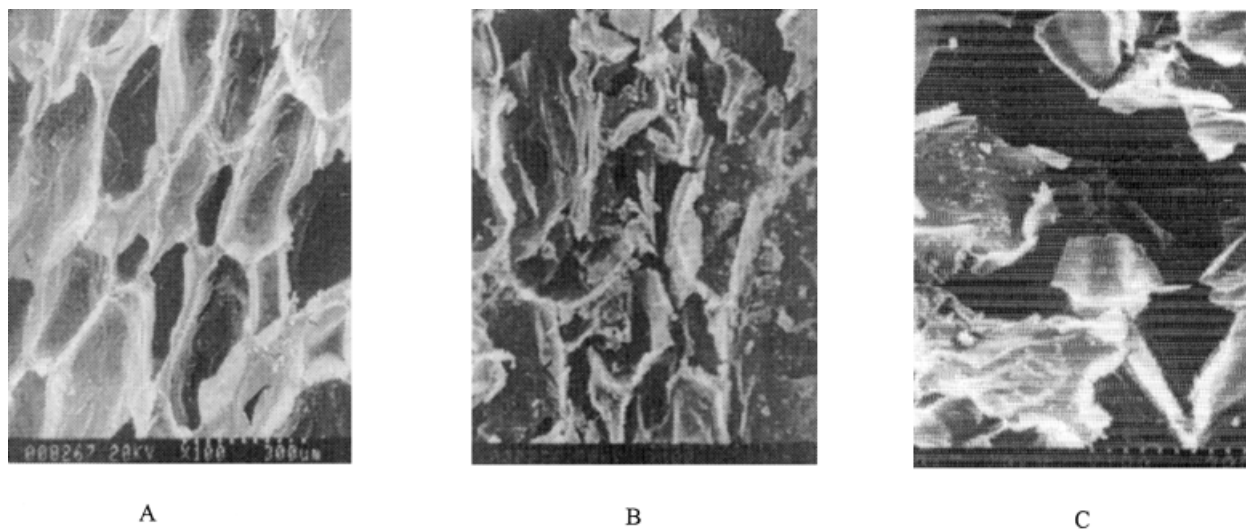


Figure 6 SEM photographs of BK-PU after different periods of soil microorganism treatment: (A) 0 months (100×), (B) 6 months (100×), and (C) 12 months (100×).

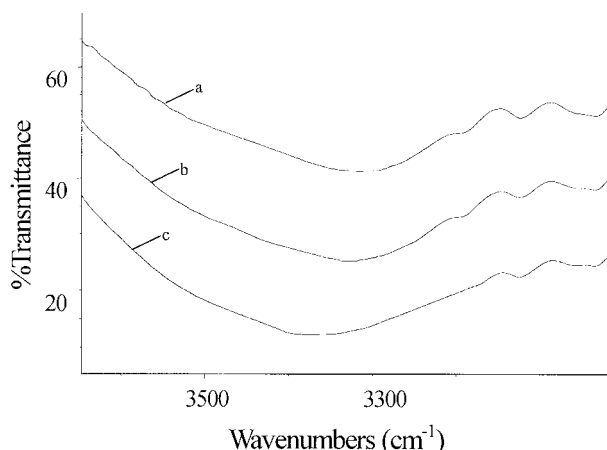


Figure 7 IR spectra of BK/CS-PU after different periods of soil microorganism treatment: (a) 0 months, (b) 6 months, and (c) 12 months.

Variations of the hydrogen bonds

Hydrogen bonds are very important to the PUF structure and controlled release. The band at 3320 cm^{-1} , assigned to the stretching vibration of the hydroxyl bond, shifted to a high wavelength in IR spectra (Fig. 7). This result indicated the weakness of intramolecular hydrogen bonds during the soil microorganism treatment. However, two discernible peaks assignable to free and hydrogen-bonded carbonyls near 1720 cm^{-1} were studied with IR absorption to characterize the molecular-level mixing of hard segments.⁹ In this study, the band of $\text{C}=\text{O}$ in urethane was divided into double bands because of the existence of hydrogen bonds in PU (Fig. 8). The band at 1730 cm^{-1} was assigned to the free carbonyl, and the lower frequency one at 1710 cm^{-1} was associated with hydrogen-bonded carbonyl, with the peak at 1600 cm^{-1} (the absorption of $\text{C}=\text{C}$ in phenyl) as a standard. The peaks of urethane and carbonyl were both weakened during soil microorganism treatment. However, no changes were obtained in IR spectra of TMP-PU under

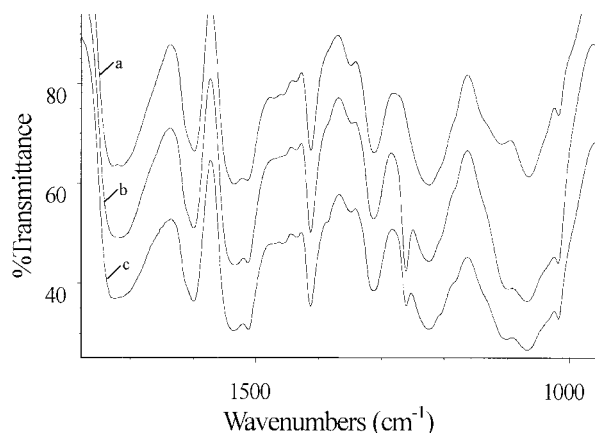


Figure 8 IR spectra of BK/CS-PU after different periods of soil microorganism treatment: (a) 0 months, (b) 6 months, and (c) 12 months.

TABLE I
Values of $(X_b)_{\text{CO}}$ for BK-PU and BK/CS-PU

Months	$(X_b)_{\text{CO}}$		
	BK-PU	BK/CS-PU	TMP-PU
0	0.314	0.289	0.34
6	0.159	0.173	0.33
12	0.139	0.137	0.33

the same conditions (date not shown). The fraction of hydrogen bonding in PU [$(X_b)_{\text{CO}}$] could be obtained as follows:¹⁰

$$(X_b)_{\text{CO}} = [1 + 1.2(A_f)_{\text{CO}}/(A_b)_{\text{CO}}]^{-1}$$

where $(A_f)_{\text{CO}}$ and $(A_b)_{\text{CO}}$ are the bond areas of free carbonyl bonds and hydrogen-bonded carbonyl, respectively. The results are listed in Table I. However, the peak at 1060 cm^{-1} was assigned to the stretching vibration of the ether bond in $\text{C}-\text{O}-\text{C}$ and $\text{C}-\text{O}-\text{H}$, which was also weakened and shifted to a high wave number (Fig. 8). The aforementioned results indicated that the hydrogen bond in PU weakened not only in the hard segments but also in the soft segments during soil microorganism treatment. It might be expected that the weakness of hydrogen bonds in PUFs could improve the release properties of PU material for fertilizer.

CONCLUSIONS

PUFs are suitable as coating materials for controlled fertilizer release and can be prepared from liquefied BK and CS. The biomass components studied had the efficacy to control the release ratio of fertilizer. When CS partially replaced BK, the release ratio could be controlled more effectively. In the last stage of release, the remaining fertilizer in PU could be released completely because the PU biomass was, to some extent, biodegradable.

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