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BIODEGRADATION OF POLY-D,L-LACTIC ACID POLYURETHANES

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ABSTRACT

The relationship between the biodegradability of poly-D,L-lactic acid (PLA) polyurethane compounds and their polymer composition was investigated. The biodegradability (weight loss) by fungi of these polyurethanes increased when: 1) the polymethylene polyphenyl polyisocyanate content of the polyurethane was reduced; 2) the molecular weight of the polyethylene glycol moiety in the polyol was increased; 3) the lactic acid content of the polyol was decreased. Proton NMR analysis of polyurethanes before and after biodegradation showed that the weight loss of PLA polyurethanes is mainly due to biodegradation of the polyol segment within the polyurethane. Measurement of oxygen consumption during cultivation of fungi indicated that only the polyol of PLA polyurethanes can be biodegraded to CO_2. However, a strain of microorganism capable of biodegrading a urethane compound (bisethylurethane of tolylene-2,4-diisocyanate) was isolated, and it was demonstrated that this compound was biodegraded in part via intermediates to tolylene-2,4-diamine.

INTRODUCTION

The biodegradability of polyurethanes has not previously been investigated in detail, but Darby et al. [1] have shown that polyester-based polyurethanes are susceptible to fungal attack. In this study, poly-D,L-lactic acid (PLA) polyurethane

compounds were synthesized, and the relationship between the biodegradability (rate of weight loss) of these polyurethanes and their polymer composition was investigated. The composition of polyurethane compounds before and after exposure to fungal attack was also analyzed by proton NMR; furthermore, measurement of oxygen consumption during cultivation of fungi was carried out to determine which fractions of the polyurethane compounds were biodegraded to CO_2. In addition, low molecular weight urethane compounds were synthesized and used to screen microorganisms capable of degrading urethane groups.

MATERIALS AND METHODS

Synthesis of Substrates

Synthesis of PLA Polyols

Poly-D,L-lactic acid (PLA) polyols were synthesized by reacting polyethylene glycol (PEG) and 2-chloropropionic acid sodium salt at 80–90°C in anhydrous DMF. The polyol consisted of PEG molecules with short terminal polylactic acid chains.

Synthesis of PLA Polyurethane Compounds

PLA polyurethane compounds were prepared by the reaction of the above polyols with polymethylene polyphenyl polyisocyanate (pMDI) and 0.3% triethylene diamine catalyst at 70°C in anhydrous conditions (Fig. 1a).

Synthesis of Urethane and Urea Model Compounds

Compound A (bisethylurethane of diphenylmethane diisocyanate) was synthesized by reacting diphenylmethane diisocyanate (MDI) with ethanol (Fig. 1b); Compound B (bisphenylurea of monomeric diphenylmethane diisocyanate) was

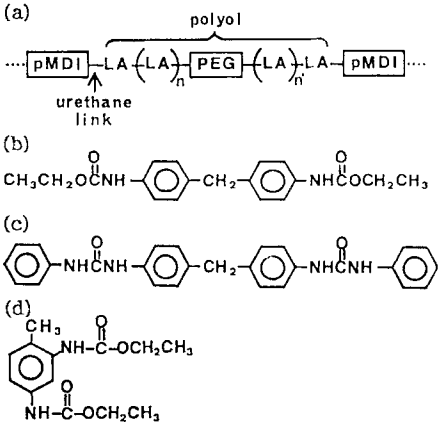


FIG. 1. Structures of (a) a poly-D,L-lactic acid polyurethane; (b) bisethylurethane of diphenylmethane diisocyanate, Compound A; (c) bisphenylurea of diphenylmethane diisocyanate, Compound B; (d) bisethyurethane of tolylene-2,4-diisocyanate, Compound C.

synthesized by reacting MDI with aniline (Fig. 1c) [2]; Compound C (bisethylurethane of tolylene-2,4-diisocyanate) was synthesized by reacting tolylene-2,4-diisocyanate with ethanol (Fig. 1d). All these compounds were synthesized in anhydrous CH_2Cl_2 at 20°C.

Cultivation and Analysis

Measurement of Biodegradation (weight loss) of Polyurethane Compounds

Polyurethane compounds were incubated at 25°C and shaking at 130 rpm in a culture medium (NH_4NO_3 0.1%, K_2HPO_4 0.07%, KH_2PO_4 0.07%, $MgSO_4$ 0.07%, yeast extract 0.05%, NaCl 0.0005%, $ZnSO_4$ 0.0002%, $FeSO_4$ 0.0002%, $MnSO_4$ 0.0002%, pH 6.5) inoculated with spores of the following fungi: *Penicillium citrinum, P. funiculosum, Aspergillus niger, Cladosporum herbarum, Trichoderma* sp., *Rhizopus stolonifer*, and *Chaetosporum globosum* (as recommended by the ASTM). Before and after cultivation, the polyurethane samples were washed in distilled water, vacuum dried at 45°C for 5 hours, and weighed. The composition of polyurethanes was calculated from proton NMR spectra (Fig. 2).

Measurement of Biochemical Oxygen Consumption of Materials

The oxygen consumption during cultivation of fungi was measured in an inorganic salts medium [according to MITI (Ministry of International Trade and Industry, Japan) Method 301C], inoculated with spores of the above fungi.

Isolation of a Microorganism Capable of Biodegrading Compound C

A strain of fungus (Strain REN-11A) capable of biodegrading Compound C was isolated from soil obtained from a polyurethane factory after enrichment cultivation in an inorganic salts medium (Compound C 0.1%, K_2HPO_4 0.2%, KH_2PO_4 0.2% NH_4NO_3 0.1%, $MgSO_4$ 0.05%, Na_2SO_4 0.001%, $FeSO_4$ 0.0004%, $ZnSO_4$ 0.0004%, $MnSO_4$ 0.0002%, pH 6.2) at 27°C and shaking at 200 rpm.

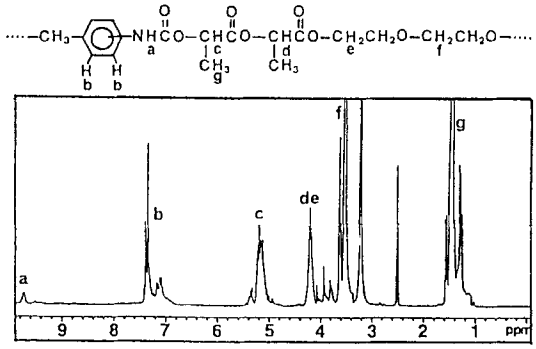


FIG. 2. ^{1}H-NMR spectrum of a PLA polyurethane (270 MHz; solvent, DMSO; 50°C).

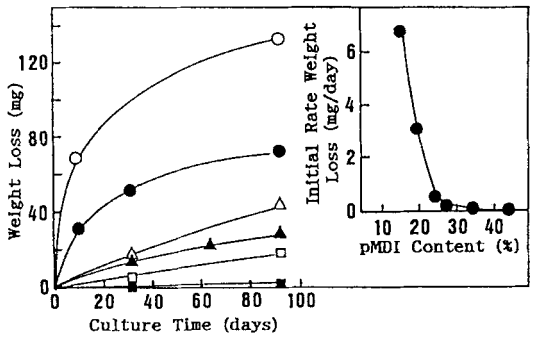


FIG. 3. Effect of the PMDI content on the weight loss of PLA polyurethanes (initial weight 200 mg). PMDI content: (○) 15.5%; (●) 19.0%; (△) 24.8%; (▲) 27.7%; (□) 34.4%; (■) 44.5%.

RESULTS AND DISCUSSION

Biodegradation of PLA Polyurethane Compounds

The rate of biodegradation (weight loss) in shaking fungal culture was less for PLA polyurethanes with higher pMDI content (Fig. 3). Polyurethanes prepared from polyols containing higher molecular weight PEG were biodegraded more rapidly than those made from polyols with lower molecular weight PEG (Fig. 4). The rate of biodegradation of polyurethanes decreased when the lactic acid content was increased (Fig. 5); however, a polyurethane compound made from a polyol containing no lactic acid (in other words, a polyethylene glycol polyurethane) was not biodegraded at all. The results of proton NMR analysis of the composition of polyurethanes before and after biodegradation are shown in Fig. 6; after 70 days the quantity of lactic acid and PEG in the polyurethane decreased by 55 and 74%, respectively, while the quantity of pMDI decreased by only 16%. This result suggests that the weight loss of the polyurethane compound is mainly due to biodegradation of the polyol segment within the polyurethane.

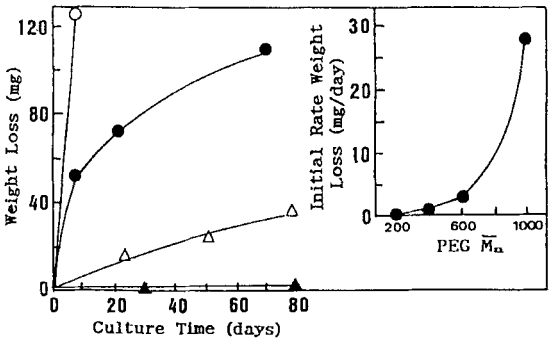


FIG. 4. Effect of the molecular weight of PEG in the polyol on the weight loss of PLA polyurethanes (initial weight 200 mg). PEG $\bar{M}_n$: (○) 1000; (●) 600; (▲) 400; (△) 200.

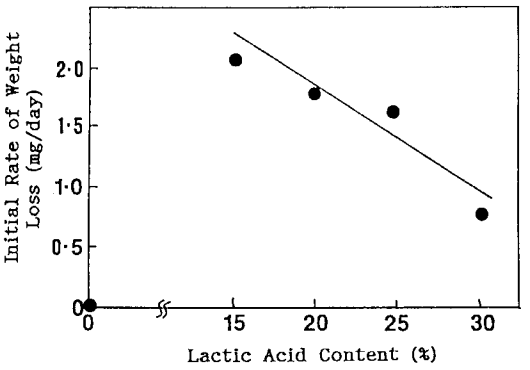


FIG. 5. Effect of the lactic acid content on the weight loss of PLA polyurethanes (initial weight 200 mg; PEG $\overline{M}_n$ = 600).

Oxygen Consumption During Cultivation of Fungi on a PLA Polyurethane, PLA, PEG, and Model Compounds

In order to determine which fractions of the polyurethane are biodegraded to CO_2, the oxygen consumption during cultivation of fungi on a PLA polyurethane, PEG, PLA, as well as Compounds A, B, and C was measured (Table 1). The polyurethane, PLA, and PEG were all readily biodegraded, while none of the urethane and urea compounds were biodegraded by the above ASTM fungi. Thus, only the polyol of PLA polyurethanes can be biodegraded to CO_2.

Biodegradation of Urethane Model Compound C

REN-11A was cultivated for 2 months in an inorganic salts medium with Compound C as the sole carbon source. After removal of the water of the culture medium by evaporation, the residual products were redissolved in CH_2Cl_2 and analyzed by GC-MS. Three compounds were detected by gas chromatography (Fig. 7). The mass spectrum of Peak 1 in the gas chromatogram (Fig. 8a) shows that this compound is likely to have been tolylene-2,4-diamine (TDA), and the mass spectra of Peaks 2 and 3 (Figs. 8b and 8c) show that these compounds could have been degradation intermediates of Compound C. The consumption of Compound C and

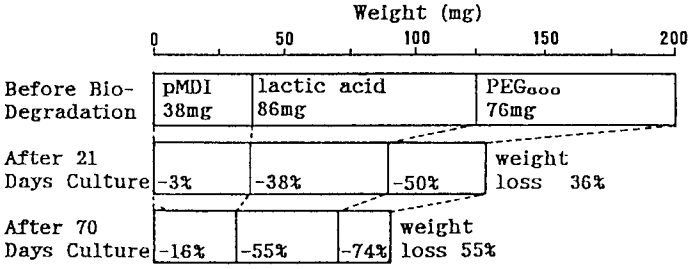
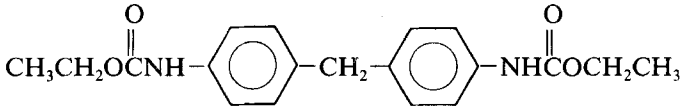
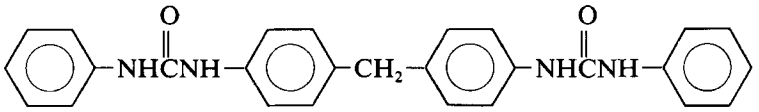
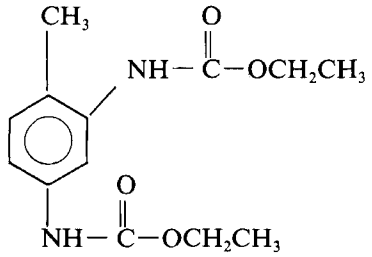


FIG. 6. Composition of a PLA polyurethane before and after biodegradation.

TABLE 1. Oxygen Consumption during Cultivation of Fungi on a PLA Polyurethane, PLA, PEG, and Urethane and Urea Compounds[a]

Substrate	% Biodegradation after 30 days culture
Poly-D,L-lactic acid polyurethane	45
Polyethylene glycol ($\overline{M}_n$ 600)	36
Poly-D,L-lactic acid ($\overline{M}_n$ 1050)	70
Compound A: 	1.5
Compound B: 	0.3
Compound C: 	0.8

[a]Measured according to MITI (Ministry of International Trade and Industry, Japan) Method 301C.

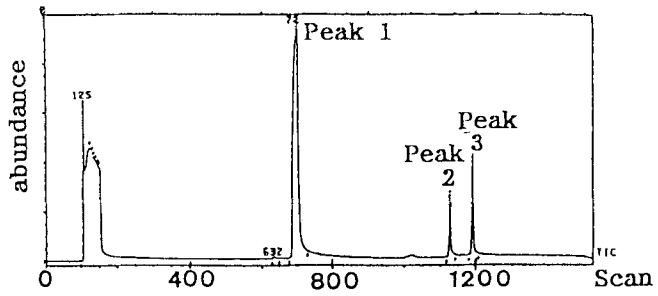


FIG. 7. Gas chromatogram of the products of degradation of Compound C by fungal strain REN-11A (column, OV-17, 0.247 mm × 30 m × 0.25 μm; carrier gas (He) flow rate, 45 mL/min).

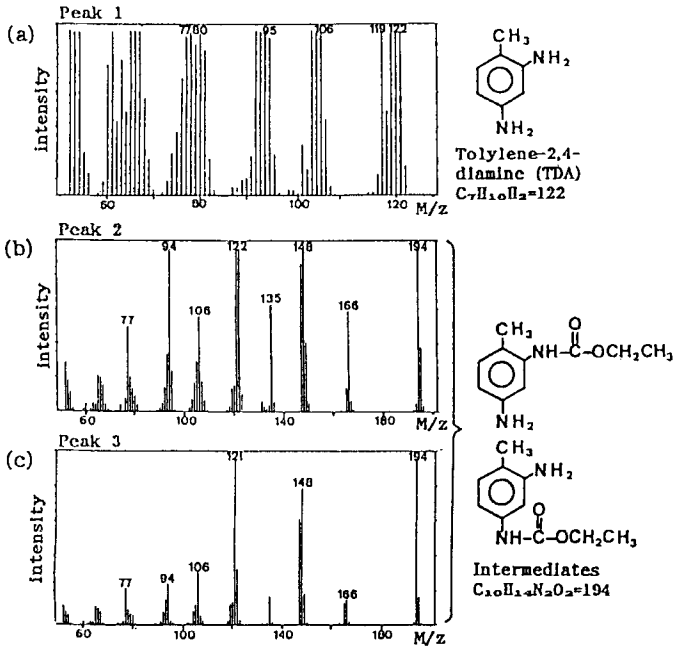


FIG. 8. Mass spectra of the compounds detected in the gas chromatogram of Fig. 7 (ion voltage, 70 eV; ion source temperature, 240°C).

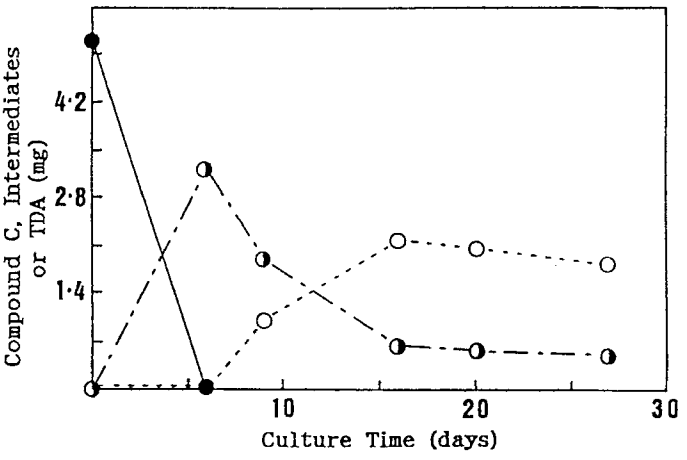


FIG. 9. Consumption of Compound C and accumulation of degradation products by fungal strain REN-11A (HPLC conditions: column, ODS 3C18, 4 × 50 mm; mobile phase, acetonitrile–water (50:50 v/v), flow rate 0.5 mL/min; UV detection at 225 nm). (●) Compound C; (◑) intermediates; (○) tolylene-2,4-diamine (TDA).

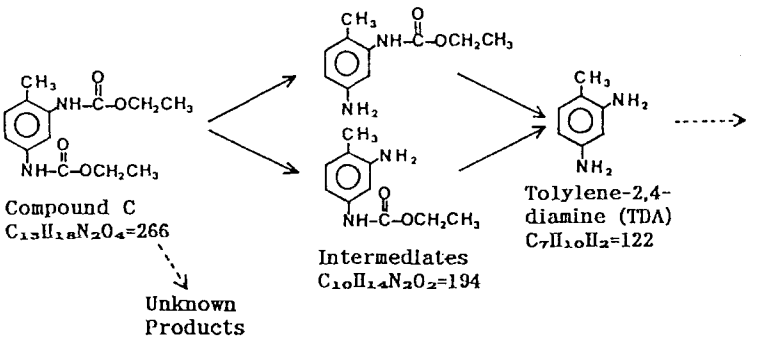


FIG. 10. Postulated pathway for degradation of bisethylurethane of diphenylmethane diisocyanate (Compound C).

the accumulation of the intermediates and TDA over time were analyzed by HPLC (Fig. 9). Compound C was completely consumed within 6 days of culture, and about 62% of Compound C accumulated as intermediates. Between 6 and 16 days of culture, the amount of intermediates decreased; the amount of accumulated TDA roughly corresponded to the amount of intermediates consumed. After 16 days, the amount of TDA decreased slightly. It seems likely, therefore, that degradation of Compound C occurs according to the scheme shown in Fig. 10.

CONCLUSION

The rate of weight loss of poly-D,L-lactic acid (PLA) polyurethane compounds in shaking fungal culture increased when: 1) the polymethylene polyphenyl polyisocyanate (pMDI) content of the polyurethane was reduced; 2) the molecular weight of the polyethylene glycol (PEG) moiety in the polyol was increased; 3) the lactic acid content of the polyol was increased. Proton NMR analysis revealed that the weight loss of the polyurethane was mainly due to biodegradation of the PEG and lactic acid of the polyol. Measurement of oxygen consumption during cultivation of fungi indicated that only the PEG and PLA fractions of the polyol in PLA polyurethanes were biodegraded to CO_2, while the pMDI fraction was not biodegraded.

A strain of microorganism capable of biodegrading a urethane compound (bisethylurethane of tolylene-2,4-diisocyanate) was isolated, and it was demonstrated that this compound was biodegraded in part via intermediates to tolylene-2,4-diamine (TDA). Therefore, there is a possibility that urethane groups within polyurethanes can be biodegraded.

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[2] T. M. Chapman, *J. Polym. Sci., Polym. Chem. Ed., 27*, 1993 (1989).