Elastomer
Vol. 34, No. 4, pp. 292~298(1999)

Degradable Oligolactide Terminated PTMG Based Polyurethanes

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(Received May 31, 1999)

ABSTRACT : Lactide oligomer with number averagae molecular weight of 460 was synthesized and reacted with poly(oxyteramethylene)glycol(PTMG, Mn=650) to obtain oligolactide oligomer-terminated PTMG. Polyurethanes were synthesized from the oligolactide-terminated PTMG, 4,4′-diphenylmethane diisocyanate, and 1,4-butanediol. The mechanical and thermal properties of the polyurethanes and PTMG based polyurethane as control were measured by means of DSC and tensile tester. Degradation behavior of these polyurethanes put into a compost was evaluated by variation of mechanical properties, surface state, and weight loss. Modulus and weight significantly decreased with increasing time. The surface of the oligolactide polyurethane put into the compost during 6 weeks had a number of voids. On the other hand, These properties of the PTMG based polyurethane as control did not change. These results suggest that the novel polyurethanes incorporated oligolactide easily degrade under biodegradable condition.

Keywords : polyetherurethane, oligolactide, oligolactide-terminated PTMG, biodegradable, mechanical properties.

I. Introduction

Polyurethanes are extensively employed to industrial materials as foams, elastomers, coatings, adhesives, and so on. Degradable polyurethane is now attracting much interest in a view of environmental protection. Polyurethanes were susceptible to biodegradation by microorganisms. Biodegradable polyurethanes are developed by use of polyester glycols prepared from ethylene glycol and lactic acid, and derived from biological products.[1-6] Kobayashi[3] and coworkers reported that polyurethanes prepared from copolyesters of D,L-lactic acid with caprolactone were biodegradable. Seppala has synthesized polyurethanes with hydroxyl-terminated copolymer of lactic acid and 1,4-butanediol. These polyurethanes were degraded by hydrolysis with buffer solution of pH 7.4.[5,6]

However, polyester glycols derived from biological products are not able to mass production and very expensive. Polyurethanes with a large amount of lactic have weak mechanical properties than general-purpose polyurethanes.

In this paper, we synthesized polyurethane elas-

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tomers contained oligolactide as a degradable moiety in order to give biodegradability to general-purpose polyurethanes. The polyurethanes were prepared from poly(oxytetramethylene-co-L-lactide) as a soft segment and evaluated its degradation behavior.

II. Experimental

1. Materials

Preparation of Oligolactide L-lactic acid was heated at 110℃ for 10 hours to obtain oligolactide. The extent of reaction was determined by the titration of acid groups. Number-average molecular weight and molecular weight ditribution were determined by acid value number and GPC, respectively.

2. Preparation of Oligolactide-terminated PTMG

Oligolactide-terminated poly(oxytetramethylene) glycols were prepared from poly (oxy tetra methylene) glycol (PTMG : Mn=650) and oligolactide at 150℃ for 30 h under reduced pressure. The reactant ratio, [COOH]/[OH], was 1. The number average molecular weight and molecular distribution were also determined. Fig. 1 shows the synthetic scheme of oligolactide-terminated PTMG.

3. Preparation of Polyurethanes (PUs)

PUs were prepared from the oligolactide-terminated PTMG, 4,4′-diphenylmethane diisocyanate (MDI), and 1,4-butanediol (BD) as a chain extender by the prepolymer method. Isocyante-terminated prepolymer was prepared from the oligolactide-terminated PTMG and MDI with reactant ratio, [NCO]/[OH], of 2.0 at 70℃ for 3h under nitrogen atmosphere.

The prepolymer and BD were well-mixed at NCO Index, [NCO]/[OH], of 1.05 for 90s and the viscous product was poured into a mold heated at 110℃ for 24h. Then PUs with 0.1mm thickness were obtained. PTMG based PU as a reference

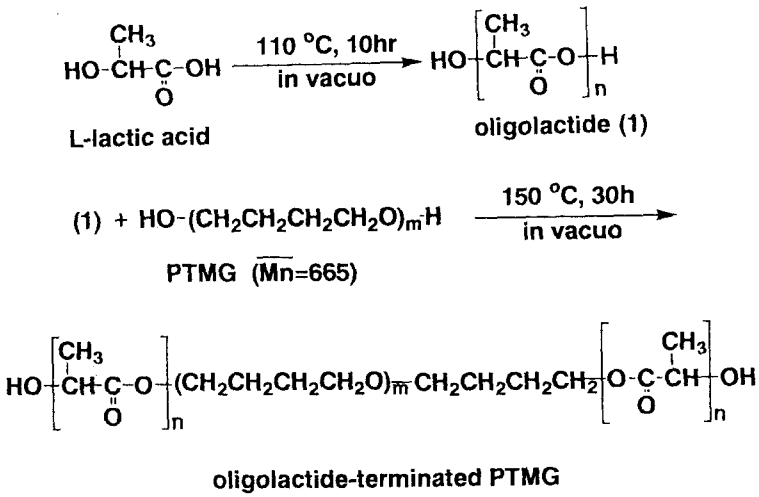

Fig. 1. Synthetic Scheme of Oligolactide-terminated PTMG.

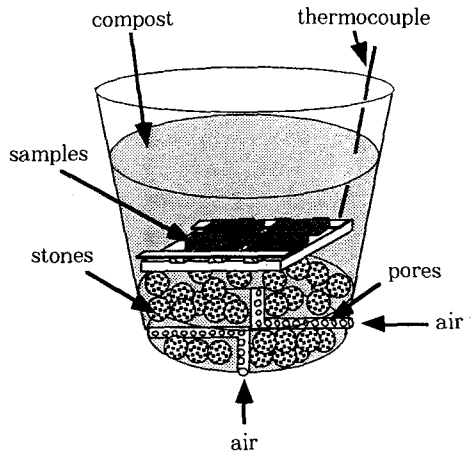

Fig. 2. Biodegradable testing Apparatus.

sample was also prepared by using PTMG(Mn= 994) instead of oligolactide- terminated PTMG.

4. Evaluation of Degradability of PUs

These PUs were put into the composts which consisted of garbage and leaf mold by use of apparatus shown in Fig. 2. Each sample size was 50×20×0.1mm. Air was bubbled into the compost during test. Temperature during test was 23-30℃ in the daytime and 18-25℃ in the night time. Time dependence of the degradation was observed by the periodic measurement of weight, modulus, and surface behavior by SEM analysis.

5. Characterization of PUs

GPC chromatograms were measured by means of GPC (Shimazdu LC-6A, Column of Shim-pack GPC802+803+803, Japan). Dimethyl formamide was used as an eluting solution.

FT-IR spectra were obtained by using a JASCO FT-IR-7000 spectrometer (Japan). Swelling behavior was measured with benzene at 50℃. Thermograms were recorded with the aid of a

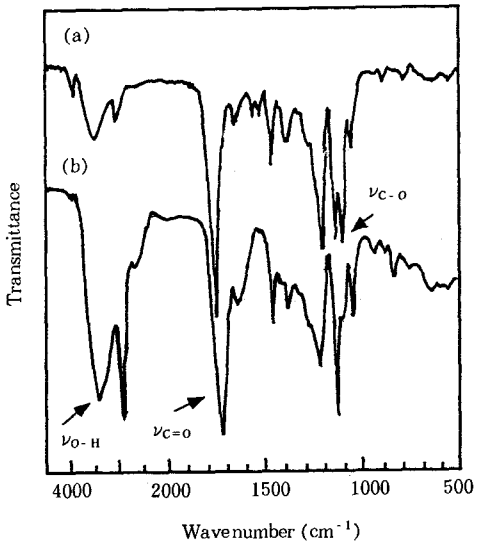

Fig. 3. FT-IR spectra of oligolactide (a) and L-lactic acid (b).

SEIKO DSC-210 (Japan) at a heating ratio of 20℃ / min under nitrogen atmosphere.

Tensile tests were carried out with Instron type tensile tester (Shimadzu AGS-100A, Japan) at 50℃. Strain rate was 0.33/min. Surface was observed by SEM (JEOL JSM-T100) with accelerated voltage of 25KV.

III. RESULTS AND DISCUSSION

1. Preparation of Oligolactide and Oligolactide-terminated PTMG

With increase of condensation reaction time, the acid value of the reaction product was decreased. Light yellowish viscous product was obtained 10 at h. Number average molecular weight calculated from acid value number was 460. Fig. 3 shows FT-IR spectra of the product and L-lactic acid. Peak intensity of O-H stretching band was as strong as that of C=O stretching band in the spec-

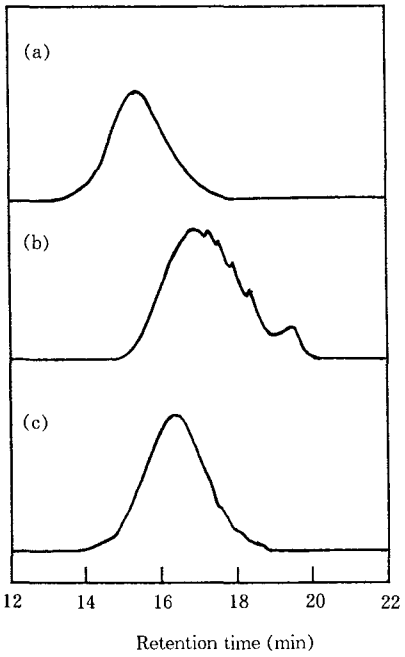

Fig. 4. GPC chromatograms of oligolactide-terminated PTMG (a), ologolactide (b), and PTMG (c).

tra of L-lactic acid. On the other hand, peak intensity of O-H stretching band was decreased and C-O stretching band assigned to ester group appeared. These results indicate that oligolactide was produced. Fig. 3 shows GPC chromatograms of oligolactide, oligolactide-terminated PTMG, and PTMG. The oligolactide synthesized had a number of chain length compounds as shown in Fig. 3. Concentration of carboxyl groups in the oligolactide was 2.3×10^{-3}mol/g. The number average molecular weight of the product was 463, that is, the average-chain length was hexamer. After the reaction of the oligolactide wtih PTMG, the product was high viscous material. The peak of oligolactide in GPC of the product disappeared and the peak of the product was lower retention time than PTMG used. These results indicate that the product has higher molecular weight. The average molecular weight determined by hydroxyl value was 1360.

2. Preparation and Properties of Polyurethanes (PUs)

The general purpose PTMG-MDI-BD PU as control was prepared from PTMG with the number-average molecular weight of 994. The oligolactide-PU contained oligolactide residue of 33wt%. Table 1 shows appearance and some properties of these PUs. Both PUs were colorless and transparent elastomers. Gel fractions of both PUs were over 97%. Degree of swelling oligolactide-PU and PTMG-PU in benzene was 2.44 and 1.44 respectively.

DSC thermograms were shown in Fig. 5. Glass transition temperature of oligolactide-PU and PTMG-PU was 5.2℃ and -62.0℃ respectively. Transition temperature of aggregation state of hard segment for oligolacte-PU and PTMG was 161.3℃ and 126.3℃, respectively.

Table 1. Appearance and properties of polyurethanes

Sample	Concentration of oligolactide(%)	Appearance	Gel fraction (%)	Degree of swelling	Young's modulus (MPa)	Tg (℃)
Oligolactide-PU	33	Colorless transparent leathery	98.2	2.44	10.4	5.2
PTMG-PU	0	Colorless transparent rubbery	97.8	1.24	8.6	-52.0

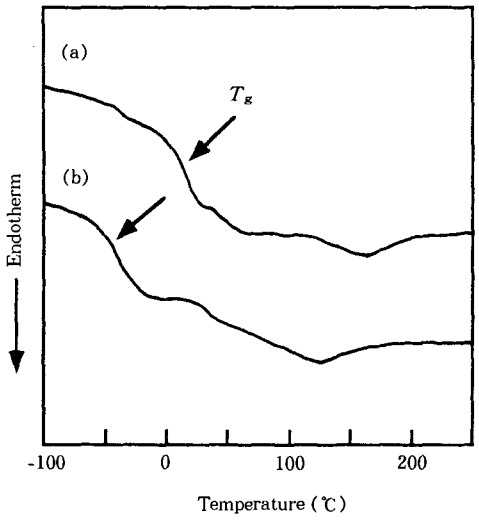

Fig. 5. DSC thermograms of oligolactide-terminated PTMG-PU (a) and PTMG-PU (b).

Fig. 6 shows stress-strain curves of PUs. Young's modulus, tensile strength and strain at break of the oligolactide-PUE were higher than those of PTMG-PUE. Modulus of oligolactide-PU was similar to that of PTMG-PU upto strain of 100% and larger over strain of 100%. These results suggest that the incorporation of rigid oligolactide into flexible PTMG occurred rigid soft segments and strengthened aggregation of chains.

3. Degradability of PUs in Compost

Both PUs degraded in the compost were transparent same as the original PUs. Fig. 7 shows the degradation behavior observed by the SEM. The surface of oligolactide-PU was smooth at initial stage, but became uneven after 2 weeks. Then erosion succeeded further with aging time. A number of voids with diameter from 1cm to 5cm were observed after 6 weeks. On the other hand, the surface of PTMG-PU showed no change after 6 weeks. Fig. 8 and 9 show dependence of the rela-

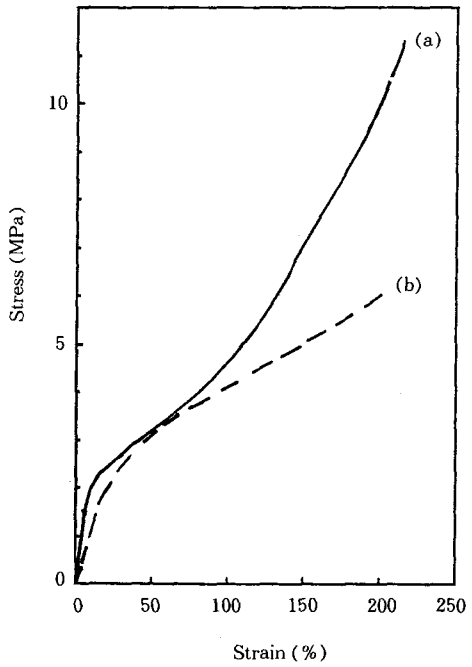

Fig. 6. Stress-strain cureves of oligolactide-terminated PTMG-PU (a) and PTMG-PU (b).

tive modulus, ratio of modulus at any time to the initial modulus, and the relative weight on degradation time respectively. Relative modulus of the oligolactide-PU decreased suddenly with increase of time and was 58% after 6 weeks, but that of PTMG-PU showed little change. Relative weight of oligolactide-PU was constant until the initial 2 weeks, and then decreased to 97% after 6 weeks. This amount of decrease at 3% equals to degradation of 6% in oligolactide contained. However, the relative weight of PTMG-PU hardly changed. These behaviors agree with the time dependence of formation of void observed by SEM. These results suggest that degradation of the oligolactide-PU in the compost was initiated by the cleavage of ester links of oligolactide as biodegradable moiety fol lowed by elusion of lower molecular weight com-

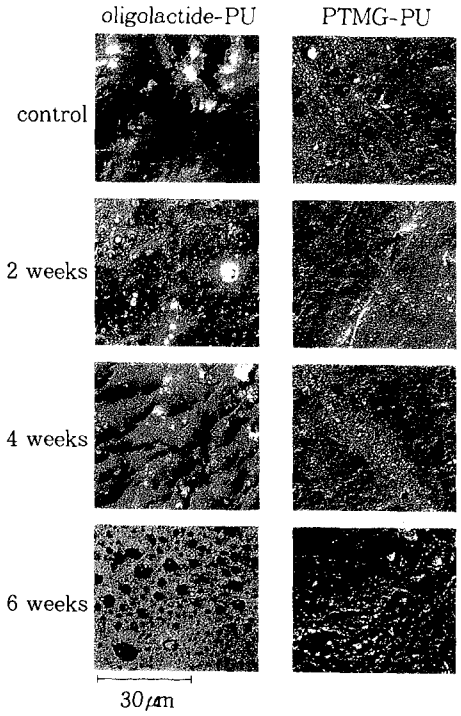

Fig. 7. Degradable behavior observed by SEM.

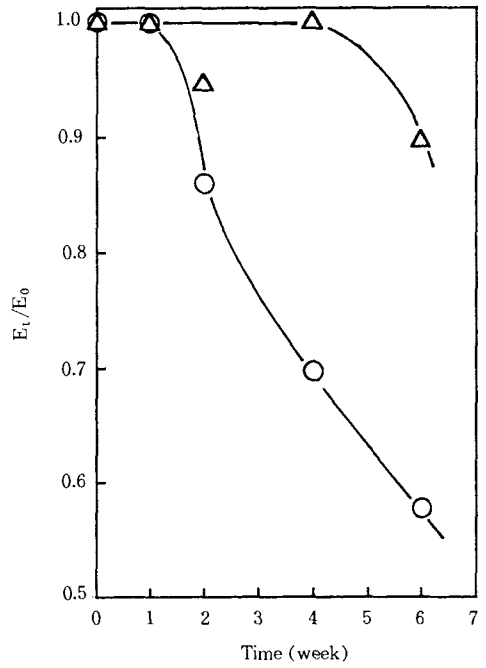

Fig. 8. Dependence of relative modulus, Et/Eo, on degradation time oligolactide-terminated PTMG-PU, PTMG-PU Et : Current modulus, Eo : initial modulus.

ponents. Seppala and coworkers[5,6] reported that PUs based coplymer of lactic acid and caprolacton which contained over 76wt% lactide residue decreased up to 20wt% of initial weight into the phosphoric acid buffer solution at pH 7.4 after 70 days, and PU contained below 65% lactide residue did not degraded significantly. These PUs had weak mechanical properties. In contrast to Seppala's resluts, the novel PU synthesized had better mechanical and degradable properties in spite of low lactide content.

IV. Conclusions

We synthesized PU consisting of poly (oxytetramethylene-co-L-lactide) as a soft segment and observed its degradation behavior. The mechanical properties and degradation behavior of PU was compared with PTMG based PU. The degradation behavior was evaluated by changes of surface observed by SEM, mechanical properties, and weight loss. While PTMG based PU was not changed, the surface of oligolactide based PU was eroded considerably, and modulus and tensile strength decreased after the degradation test for 6 weeks. These results indicate that degradation was started at oligolactide moiety, followed by decrease of molecular weight of the oligolactide-PU, and eroded from the surface. The novel PUs incorporating oligolactide moiety easily degrade under biodegradable conditions.

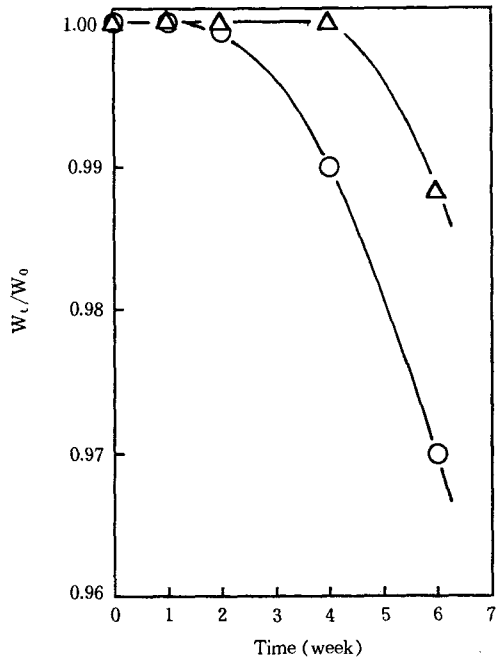

Fig. 9. Dependence of relative weight, Wt/Wo, on degradation time oligolactide-terminated PTMG-PU, PTMG-PU Wt : current weight, Wo : initial weight.

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