Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Härkönen, Mika , Hiltunen, Kari , Malin, Minna and Seppälä, Jukka V.(1995) 'Properties and Polymerization of Biodegradable Thermoplastic Poly(Ester-urethane)', Journal of Macromolecular Science, Part A, 32: 4, 857 — 862

To link to this Article: DOI: 10.1080/10601329508010297

URL: http://dx.doi.org/10.1080/10601329508010297

J.M.S.—PURE APPL. CHEM., A32(4), pp. 857-862 (1995)

PROPERTIES AND POLYMERIZATION OF BIODEGRADABLE THERMOPLASTIC POLY(ESTER-URETHANE)

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ABSTRACT

Aliphatic polyesters, such as poly(lactic acids), need high molecular weight for acceptable mechanical properties. This can be achieved through ring-opening polymerization of lactides. The lactide route is, however, relatively complicated, and alternative polymerization routes are of interest. In this paper we report the properties of a polymer made by a two-step process: first a condensation polymerization of lactic acid and then an increase of the molecular weight with diisocyanate. The end product is then a thermoplastic poly(ester-urethane). The hydroxyl-terminated prepolymer was made with condensation polymerization of L-lactic acid and a small amount of 1,4-butanediol. The polymerization was performed in the melt under nitrogen and reduced pressure. The preparation of poly(ester-urethane) was done in the melt using aliphatic diisocyanates as the chain extenders reacting with the end groups of the prepolymer. The polymer samples were carefully characterized, including preliminary degradation studies. The results indicate that this route to convert lactic acid into thermoplastic biodegradable polymer has high potential. Lactic acid is converted into a mechanically attractive polymer with high yield, which could make the polymer suitable for high volume applications. The mechanical properties of the poly(ester-urethane) are comparable with those of poly(lactides). Capillary rheometer measurements indicate that the polymer is processible both by injection molding and extrusion.

INTRODUCTION

It has become a rather widely adopted opinion that biodegradable polymers have a well-grounded role in solving the waste problem. When composting of waste becomes more common, normal "stable" thermoplastics can cause problems in some applications, especially when those plastics are combined with otherwise compostable material. However, at present the relatively poor properties and high price of compostable plastics make their utilization in volume applications unattractive and practically impossible.

The feasibility of production processes and the possibility to use renewable raw materials have made lactic acid an attractive monomer for biodegradable polymers. However, poly(lactic acid) needs a relatively high molecular weight to have acceptable mechanical properties in many applications [1]. Conventional condensation polymerization of lactic acid does not increase the molecular weight enough, and the yield of cyclic side products, such as lactides, is often too high. Acceptable molecular weights can be achieved through ring-opening polymerization of lactides. This route is, however, relatively complicated due to the multistep process from lactic acid through a lactide intermediate into the final poly(lactide), which makes the total yield rather low. Therefore, alternative polymerization routes are of interest.

In this paper, properties of a biodegradable thermoplastic poly(ester-urethane) based on lactic acid are reported. The polymer is produced by a two-step process: first, a condensation polymerization of lactic acid and then an increase of the molecular weight with diisocyanate. In the literature there have been only a few publications [2–4] where resembling polymers have been reported. For example, Hori et al. [2] published an article describing the synthesis of poly(ester-urethane) from poly(3-hydroxybutyrate) segments.

EXPERIMENTAL

In the preparation of poly(L-lactic acid) prepolymer, a mixture containing 98 mol% L-lactic acid and 2 mol% 1,4-butanediol was condensation polymerized in a rotation evaporator under a nitrogen stream and reduced pressure. Stannous octoate was used as a catalyst.

The poly(ester-urethane) was prepared from 250 g prepolymer and 20 mL 1.6-hexamethylene diisocyanate in a stirred glass reactor in melt under a nitrogen atmosphere.

The molecular weights were analyzed with GPC (Waters) at room temperature using polystyrene standards. In addition, the poly(L-lactic acid) prepolymer was characterized with ^{13}C NMR (Varian Unity 400, working at 100,577 MHz) to quantitatively determine the amount of hydroxyl end groups, lactic acid, and lactide residues. FT-IR analysis were done with a Nicolet Magna-IR Spectrometry 750. The mechanical properties were determined from compression-molded specimens with an Instron 4204. The DSC analysis were made by a Polymer Laboratories DSC and DMTA analysis by a Perkin-Elmer DMA 7. Rheological measurements were done with a capillary rheometer (Göttfert Rheograph) having a die of 20:1.

RESULTS AND DISCUSSION

The poly(L-lactic acid) prepolymer had a number-average molecular weight of 4500 g/mol measured with GPC. The prepolymer had 5.7 wt% L-lactide and 5.6 wt% L-lactic acid residues measured with ^{13}C NMR. The hydroxyl termination of the prepolymer was confirmed and quantitatively measured with ^{13}C NMR. The number-average molecular weight calculated from the ratio between main chain carbons and chain ends was 2100 g/mol.

The product poly(ester-urethane) had a number-average molecular weight of 32,000 g/mol (with GPC), and according to FT-IR analysis it did not contain any free isocyanate groups. The polymer contained 1.6 wt% L-lactide residue, but no L-lactic acid was detected. The total conversion of L-lactic acid to poly(ester-urethane) was about 96 mol%.

Mechanical properties of this poly(ester-urethane) (PEU) compared to some other relevant polymers are seen in Fig. 1. The tensile strength and modulus of PEU are very close to the corresponding values of poly(L-lactide) made by the

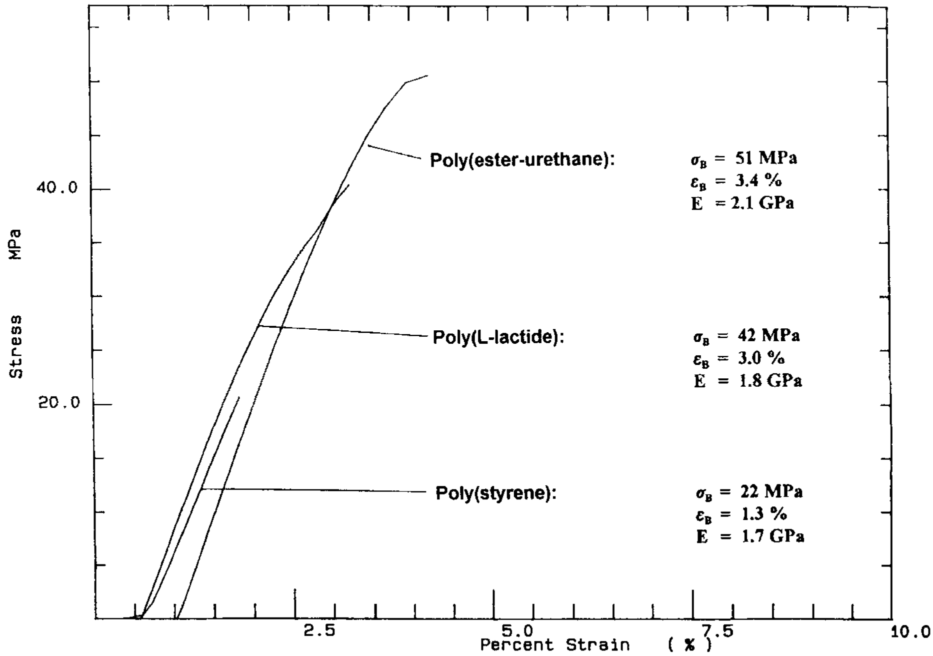

FIG. 1. Stress-strain curves and tensile properties of compression-molded test specimens of the poly(ester-urethane) and some reference materials.

ring-opening route. Typically these aliphatic polyesters resemble polystyrene, although polystyrene is more brittle.

DSC analysis shows that PEU is a totally amorphous polymer having a clear glass transition temperature (T_g) at 53°C. The three-point bending DMTA analysis in Fig. 2 shows that the storage modulus drastically decreases at a temperature of about 50°C, and that the T_g measured from the peak value of tan δ is 62°C. Thermal analysis indicates that PEU loses its mechanical properties at temperatures above 50°C.

Capillary rheology analysis (Fig. 3) shows that PEU is thermoplastic. It is processible by conventional methods. The melt viscosity is suitable for injection molding at a temperature of 210°C in typical shear rates of injection molding (2000 L/s). At 180°C the melt viscosity is at an acceptable level for extrusion. Thermal degradation may be partially responsible for the marked decrease in the melt viscosity between 180 and 210°C.

According to degradation studies of poly(urethane) mentioned in the literature [5, 6], it can be assumed that degradation behavior is relatively close to the corresponding properties of the prepolymer used. The preliminary hydrolysis test series showed that poly(ester-urethane) is hydrolytically degradable, though the degradation seems to be slower than that of poly(L-lactide). For example, the number-average molecular weight of a PEU sample decreased during hydrolysis at 37°C (pH 7) from an initial 49,000 g/mol to 43,000 g/mol in 1 week and to 5,000 g/mol after 8 weeks (Figure 4). The degradation behavior resembles that of poly(L-lactide) [7], and practically no weight loss was observed during the test period. However, these hydrolysis tests were only preliminary, and no final conclusions about degradation can be made.

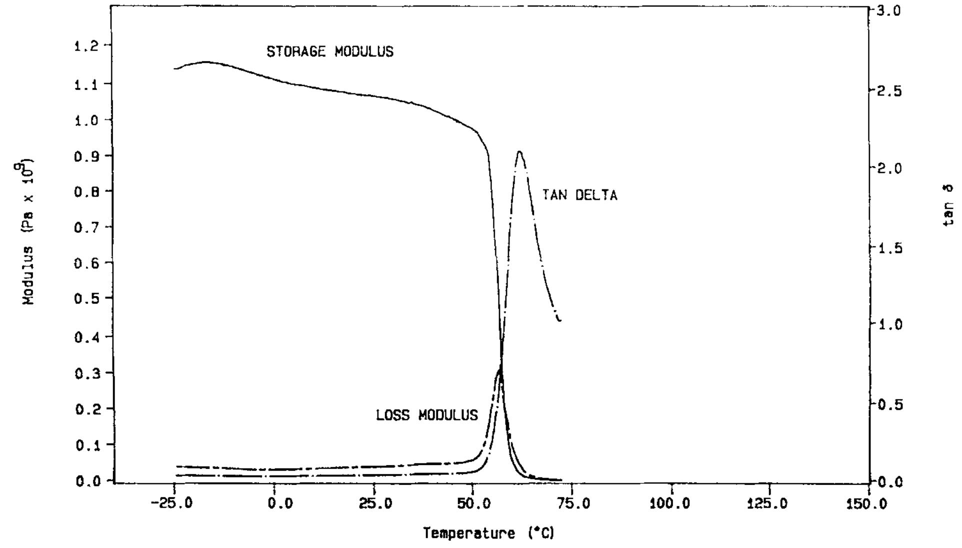

FIG. 2. The three-point bending DMTA analysis of the poly(ester-urethane).

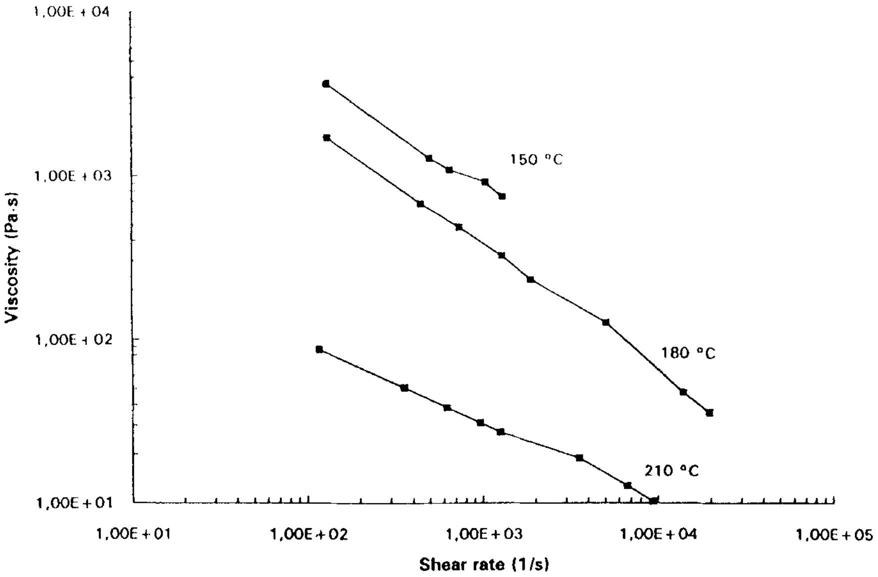

FIG. 3. Capillary rheometer analysis of the poly(ester-urethane).

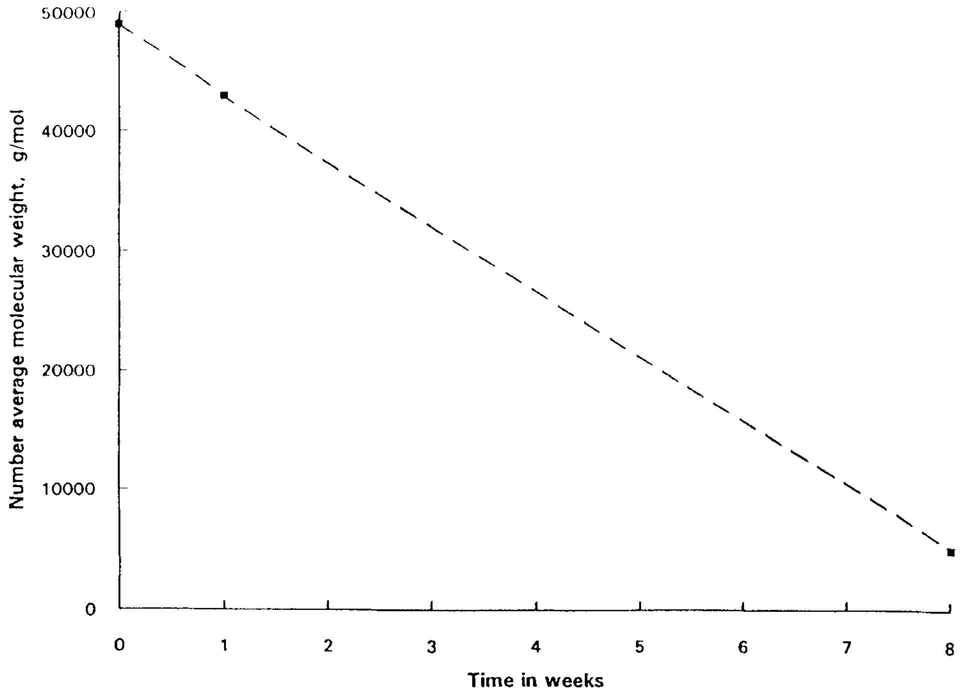

FIG. 4. Decrease of the number-average molecular weight of the poly(ester-urethane) during hydrolysis at 37°C and pH 7.

CONCLUSIONS

According to this study, this polymerization route to a thermoplastic biodegradable polymer based on lactic acid has high potential. Lactic acid can be converted into a mechanically attractive polymer with high yield (>95%), and the polymerization is technically feasible, at least on a laboratory scale.

The mechanical properties of this poly(ester-urethane) are comparable to those of poly(lactide)s made through a ring-opening route. The rheological measurements indicate that the polymer is processible with conventional methods such as injection molding and extrusion. The polymer loses its stiffness at about 50°C, which can be too low for many applications. The preliminary degradation studies indicate that the polymer is hydrolytically degradable.

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