

Effect of molecular weight distribution on the elasticity of melt of biodegradable poly(ester-urethane)

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ABSTRACT

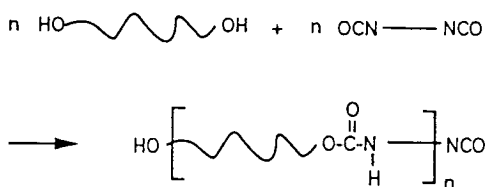
Biodegradable thermoplastic poly(ester-urethane)s were synthesized from lactic acid based polyester prepolymer and 1,6-hexamethylene diisocyanate. Polymerization chemistry of the poly(ester-urethane) indicates that the changes of molecular weight distribution result from long chain branching and initial stage of cross linking.

The effects of molecular weight distribution on rheology of poly(ester-urethane) melts have been studied with dynamic mechanical thermal analysis (DMTA) of molten samples. The results indicate clear correlation between the broadness of molecular weight distribution and melt elasticity of the polymer samples. The melt elasticities of poly(ester-urethane) and linear poly(L-lactide) showed marked differences. The results support the suggestions that the changes in molecular weight distribution of poly(ester-urethane)s are caused by long chain branching.

INTRODUCTION

Aliphatic polyesters, such as poly(L-lactide) are one marked group of synthetic biodegradable polymers which can be produced in large scale. In this work lactic acid based poly(ester-urethane) has been studied. The hydroxyl terminated poly(L-lactic-acid) prepolymer units are coupled together through urethane bonds /1/.

The number average molecular weight of prepolymers and final poly(ester-urethane) are



typically about 4000 g/mol and 40000 g/mol respectively, which indicates that on average 10 prepolymer units are coupled. The polydispersity of the poly(ester-urethane) are typically over 3, and with certain polymerization conditions the polydispersity can be increased to more than 10 /2/. Even cross-linked polymers can be obtained.

The chemistry of poly(urethane) synthesis /3/ suggests that the broadness of molecular weight distribution is most probably caused by inter-chain reactions between urethane bonds and terminal isocyanate groups. These reactions can lead to high degree of cross-linking. However, if the degree of the inter-chain reactions can be controlled, the polymer retains its thermoplasticity and mainly long chain branching is obtained.

One disadvantage of linear polyesters, such as poly(L-lactide), are relatively low melt elasticity, which can cause problems in certain fabrication processes using extrusion techniques. The poly(ester-urethane) studied in this work is composed over 90 w-% of lactic acid units. Therefore comparisons with poly(L-lactide) can be made. The initial processing experiments of the poly(ester-

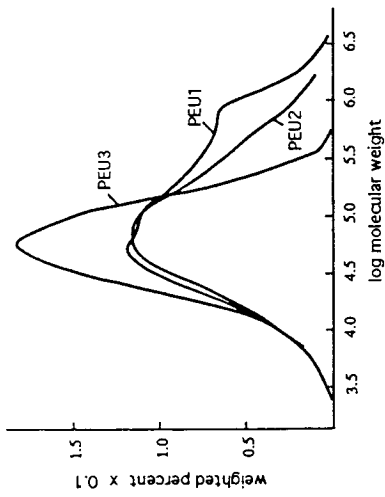


Figure 1a. Molecular weight distribution of the poly(ester-urethane)s.

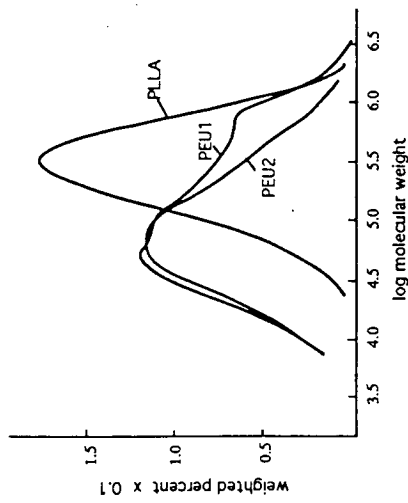


Figure 2a. Molecular weight distribution of poly(ester-urethane)s and poly(L-lactide).

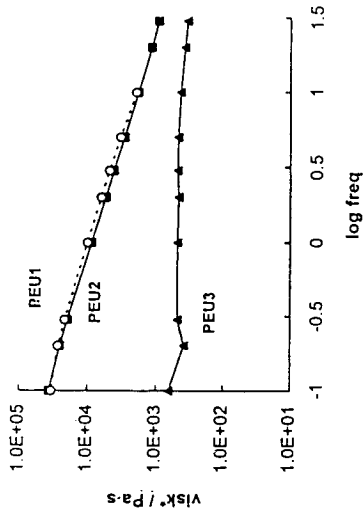


Figure 1b. Viscosity of poly(ester-urethane)s vs. frequency (T=160°C).

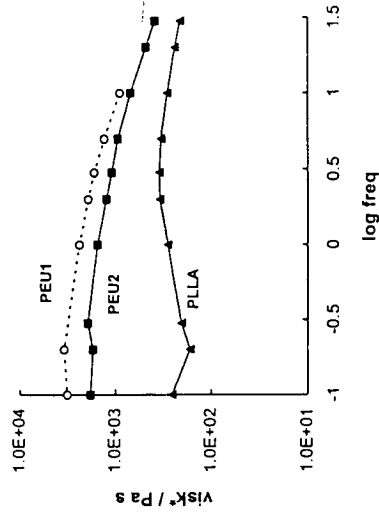


Figure 2b. Viscosity of poly(ester-urethane)s and poly(L-lactide) vs. frequency (T=180°C).

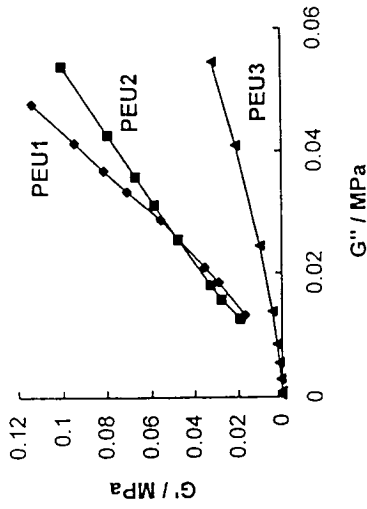


Figure 1c. G' vs. G'' of the poly(ester-urethane)s (T=160°C).

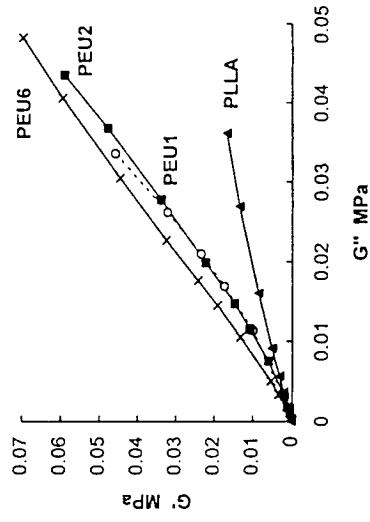


Figure 2c. G' vs. G'' of poly(ester-urethane)s and poly(L-lactide) (T=180°C).

urethane) have shown that the polymer melt is fairly elastic and it has processing properties resembling long chain branched polymers.

Our aim of this work was to study the rheology of polymer melts in order to deepen our understanding on processability of this material. In addition, the causes for the observed differences of molecular weight distribution are studied.

EXPERIMENTAL

Hydroxyl terminated poly(L-lactic acid) prepolymer was manufactured by condensation polymerisation of L-lactic acid and 2 mol-% 1,4-butanediol. The poly(ester-urethane) was synthesized in melt of the prepolymer and 1,6-hexamethylene diisocyanate under mechanical agitation /2/. Several different samples of poly(ester-urethane) were synthesized, and the molecular weight and molecular weight distribution were analyzed with gel permeation chromatography (GPC) calibrated with polystyrene. The molecular weight and molecular weight distribution can be controlled by polymerization conditions and ratios of feedstock.

The rheological properties of the polymer samples were determined with Polymer Laboratories DMTA, which allows the measurements of polymer melts. The circular DMTA specimens were cut from dry compression moulded sheets of 2 mm thickness. The dynamic shear frequency of the measurements varied typically from 0.1 1/s to 30 1/s.

RESULTS AND DISCUSSION

Figure 1a shows how the molecular weight distribution can be controlled with polymerization conditions. The polymer sample PEU3 is expected to be a linear poly(ester-urethane) comprising of prepolymer units coupled together only from the chain ends. Comparing PEU3 to samples PEU2 and PEU1 have clearly broader molecular weight distribution which is suggested to be result of long chain branching.

As seen in Fig. 1b the samples that have a broad molecular weight distribution (PEU1 and PEU2) give clear increase in melt viscosity at low shear rates. The effect of molecular weight distribution on the elasticity

of melt can be seen in Fig. 1c. The Storage modulus (G') with constant loss modulus (G'') increased systematically with the broadness of the molecular weight distribution. Also the sample with the most broad molecular weight distribution gave slightly higher slope to the G' against G'' curve.

Similar correlations between molecular weight distribution and rheological properties can be seen also for poly(ester-urethane)s having clearly lower of molecular weight.

Fig. 2 shows the differences in molecular weight distribution and rheological properties of the poly(ester-urethane) compared to poly(L-lactide). The viscosity and elasticity of poly(ester-urethane) melts were clearly higher than corresponding values of poly(L-lactide) - despite the higher molecular weight of poly(L-lactide). Especially clear are differences in the slope of G' vs. G'' . These results refers to major differences in melt elasticity and processing properties.

Some of these rheological observations can be only result of the high polydispersity of the samples. However, in combination with the findings that uncontrolled polymerization conditions lead to cross-linking, the results of this study support the suggestions that the broadness of molecular weight distribution is caused by interchain reactions leading initially to long chain branching.

The results clearly show that rheological properties of this lactic acid based polymers can be tailored by controlling the interchain reactions during polymer synthesis. The elasticity of polymer melt can be markedly increased which makes possible to tailor markedly the processing properties of these polymers offering new possibilities for utilization of synthetic biodegradable plastic materials.

REFERENCES

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