Influence of Processing Parameters on the Degradation of Poly(L-lactide) During Extrusion

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ABSTRACT: The influence of processing conditions during melt extrusion on the degradation of poly(L-lactide) (PLLA) has been investigated. PLLA polymer was processed by melt extrusion in a double screw extruder at 210 and 240°C. For each extrusion temperature, two screw rotation speeds, 20 and 120 rpm, were used. To investigate the influence of moisture on the thermal degradation during processing, the PLLA granules were dried at 100°C for 5 h and then either extruded directly or conditioned at 65% RH, 20°C for 24 h prior to extrusion. The results show that a decrease in molecular weight measured as number-average (M_n) molecular weight occurs for all combinations of process parameters used. At processing temperature of 210°C, the change in molecular weight for the dry granules was shown to be dependent on the residence time (i.e., screw rotation speed) in the melt. By changing the screw rotation speed from 120 to 20 rpm at 210°C, M_n decreased from 33,600 to 30,200 g/mol. When the processing temperature was increased to 240°C, the dry granules showed an M_n of 25,600 and 13,600 g/mol when extruded at 120 and 20 rpm, respectively. M_n for the conditioned specimens extruded at 210°C was 18,400 g/mol when processed at 120 rpm and 12,300 g/mol at 20 rpm. When processed at 240°C, 20 rpm, M_n is independent of whether the granules were dry or moist prior to extrusion. It is probably due to the fact that the degradation at 240°C is so extensive that the presence of moisture in the polymer does not contribute further to the degradation process. The stress and strain at break decreased due to degradation and were dependent on the molecular weight of the samples. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 2128–2135, 2001

Key words: PLLA; poly(L-lactide); melt-processing; thermal degradation; melt extrusion

INTRODUCTION

The environmental issues such as increasing quantities of deposited polymeric waste and increasing CO_2 levels in the atmosphere because of burning of fossil fuels have resulted in significant industrial efforts aimed at developing biodegradable and biopolymer-based materials. Poly(lactic acid) (PLA) is a biopolymer that has been studied rather extensively during the past few years. PLA is produced from lactic acid by direct polymerization or by a ring-opening polymerization from lactide in the presence of a catalyst.[1] PLA is an aliphatic polyester and is caused by the hydrolyzable backbone, which can be subjected to hydrolytic degradation, giving lactic acid as degradation product; PLA has been used in resorbable products for several years. Sutures, temporary fixation, and capsules for slow release of drugs are some of the medical applications presented in the literature.[2–6] The increasing interest in degrad-

able polymers and polymers based on renewable resources has suggested that PLA can be a suitable material for applications outside the medical field as well. It has been shown that PLA can be used for film, fibers, and nonwovens[7–11] in, for example, food and medical packaging, coverstocks in hygiene products, etc. The main part of these products is produced by different types of melt processes such as melt spinning, film blowing, or injection molding.

PLA is thermally unstable and exhibits rapid loss of molecular weight as the result of thermal treatment at processing temperatures. It has been postulated that thermal degradation mainly occurs by random main-chain scissions. Several reactions such as hydrolysis, depolymerization, oxidative degradation, and inter- and intramolecular reactions are suggested to be involved in the degradation process during thermal treatments.[12] It has previously been shown[13–17] that the thermal degradation is influenced by the presence of metals, monomers, and other impurities in the PLA and also by parameters such as processing temperature and time in the melt.[12,13,18] The reduction in molecular weight, when processed, can affect the polymer properties. However, almost all such experiments has been performed on a laboratory scale and only a few reports are available describing the effect of injection molding, melt spinning, and extrusion processes on degradation and polymer properties. If PLA is to be used as commodity plastics in the future, it is important that the influence of melt processes and processing parameters on the properties of PLA is clearly understood.

In this work, the effect of process parameters, namely, process temperature, residence time, and the inherent moisture content, on the properties of poly(L-lactide) (PLLA) has been investigated.

EXPERIMENTAL

Material and Conditioning

PLLA granules were supplied by Neste Oy, Bergå, Finland. The granules were dried at 100°C for 5 h, according to the producers' recommendations. After drying, the polymer granules were either processed directly or conditioned at 65% RH, 20°C for 24 h prior to extrusion. After the conditioning process, the moisture content of the granules measured by Karl–Fischer titration method was 0.3%, calculated on dry weight. The moisture content of the dry samples was below the detection limit of the Karl–Fischer equipment used.

Processing Conditions and Sample Preparation

A Plasticorder brabender equipped with double screws was used for melt extrusion of the PLLA polymer. The melt extrusion was performed at two temperatures (i.e., 210 and 240°C), which both lie within the limits of the producers recommendations, which is above 180°C and below 250°C for the PLLA material used. The two processing temperatures were chosen because it was the lowest and highest temperatures possible to run without too much trouble with the equipment used. In this experiment, all heating zones in the extruder were kept at constant temperature levels. The temperature was kept constant because of the very high shear rates and difficulties in melting obtained if the temperature in the first zone was kept at lower temperature with the PLLA used. For each processing temperature used, the extrusion was performed at screw rotation speeds of 20 and 120 rpm, respectively. The polymer was fed manually in small portions to keep the material from clogging before entering the heated zones in the extruder but also for keeping the polymer at the desired humidity. After extrusion, the polymer samples were granulated. The granules were stored in a desiccator over silica gel at room temperature. Parts of the granulated material were compression molded on Teflon film at 190°C into 1.7-mm-thick plates, quenched to room temperature, and then stored in a desiccator over silica gel at room temperature. The molecular weight and melt flow index (MFI) was measured on the extruded granules, whereas crystallinity and tensile properties were measured on the compression molded plates.

Melt Viscosity

The dynamic melt viscosity (η), including storage modulus (G^I) and loss modulus (G^{II}), was measured on the unextruded PLLA polymer granules by using a Rheometrics Dynamic Analyser RDA II equipment at 1 Hz and 5% deformation. Temperatures used were 210, 225, and 240°C and the measurement was started after the time necessary to obtain a molten sample in the equipment.

Size Exclusion Chromatography

The molecular weights, measured as number-average (M_n) and weight-average (M_w) molecular

weight, of the extruded samples were determined by size exclusion chromatography (SEC) in chloroform by using styragel columns. The calibration of the PLLA molecular weights was performed by using polystyrene standards.[19]

Melt Flow Index

The MFI of the samples after extrusion was determined at 180°C in a capillary viscosimeter, CAEST 6540/010. The samples were heated for 4 min and then the polymer melt flow (MFI) was determined as a function of time. A weight of 2.16 kg was used and for each sample a minimum of five measurements were made.

Differential Scanning Calorimetry

The crystallinity of the compression-molded PLLA plates was determined by differential scanning calorimetry (DSC) by using a Perkin–Elmer DSC 7. The samples were heated from 0 to 200°C at a heating rate of 10°C/min and then quenched to 0°C, and then a second run was performed. The crystallinity of the samples was determined from the enthalpy difference between melting and crystallization peaks in the first temperature scan and enthalpy of 100% crystalline PLLA (93.6 J/g).[20] Glass transition temperature (T_g) and melting temperature (T_m) were determined from both scans.

Mechanical Properties

Measurements of stress and strain at break were made on Monsanto tensile tester, type Tensiometer 10, equipment by using compression-molded specimens 1.7 mm thick, 17 mm in width, and 90 mm in length. Gauge length was 10 mm and deformation rate 50 mm/min. A minimum of four specimens was used for each sample.

RESULTS AND DISCUSSION

Processing Conditions

The moisture in the PLLA granules affected the ability to obtain a stable and trouble-free extrusion process because the granules clogged the entrance of the extruder.

The residence time of the polymer in the heated zones of the extruder was varied by using two screw rotation speeds of 20 and 120 rpm. In Table I, the residence times in the melt and the

Table I Rotation Speeds and Corresponding Residence Time in the Melt for the Extrusion Equipment Used

Screw Rotation Speed (rpm)	Minimum Residence Time (min : s)	Polymer Throughput (kg/h)
20	7 : 00	1.0
120	1 : 45	5.4

polymer throughput are given for the process parameters used. The residence time given in Table I is the shortest residence time measured at the specific rotation speed used. However, by using the lowest speed rotation of 20 rpm, not only the residence time of the melt in the extruder becomes longer compared to 120 rpm, but also the residence time distribution. This means a much longer residence time for parts of the polymer in the melt and this aspect must be considered when processing the thermally degradable PLLA material. By increasing rotation speed from 20 to 120 rpm, the clogging that occurred for the conditioned granules became a lesser problem due to the fact that transport of the granules from the heated entrance zone of the extruder was faster.

The combination of processing parameters of 240°C and 20 rpm (i.e., high temperature and long residence time) led to a massive thermal degradation, causing a very low viscosity of the extruded PLLA polymer. On the other hand, processing at 210°C at 120 rpm led to high shear rates due to high viscosity of the polymer. The high shear rates led to mechanical treatment of the polymer and a temperature increase in the melt might be the consequence. However, no temperature increase of the polymer melt was noticed in this investigation.

Molecular Changes

Number-average (M_n) molecular weights at different processing parameters are shown in Figure 1.

For the nonextruded, compression-molded samples, M_n was 40,000 g/mol. At processing temperature of 210°C, the change in molecular weight for the dry granules was shown to be dependent on the residence time (i.e., screw rotation speed) in the melt (Fig. 1). At 210°C, M_n decreased from 33,600 to 30,200 g/mol when the rotation speed was reduced from 120 to 20 rpm.
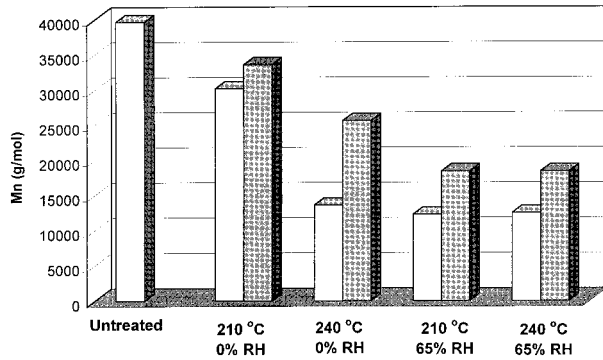
Figure 1   Molecular weight (M_n) as a function of processing conditions. White: 20 rpm; gray: 120 rpm.

At processing temperature of 240°C, the dry granules showed an M_n of 25,600 and 13,600 g/mol when extruded at 120 and 20 rpm, respectively. M_n for the conditioned specimens extruded at 210°C was 18,400 g/mol when processed at 120 rpm and 12,300 g/mol at 20 rpm. At 240°C and 20 rpm, M_n was independent of whether the granules were dry or conditioned prior to the extrusion. It is probably due to the fact that the thermal degradation at 240°C is so extensive that the moisture content in the polymer does not contribute further to the degradation process.

In the molecular weight distribution graphs in Figure 2, it can be observed that the conditioned granules extruded at 210°C and 20 rpm show a shift to lower molecular weights compared with the dry material extruded at the same processing conditions. This is probably due to a combination of regular thermal degradation in combination with the hydrolysis effect water has on the thermal degradation at 210°C. The shifts in molecular weight for samples processed at 240°C and 20 rpm is, however, independent of the moisture content. Molecular weight distribution (MWD) shows only very small differences between the different samples (Fig. 2).

For processing purposes, it is interesting to note that the thermal degradation measured as loss in M_n is larger for moisture-containing granules extruded at a 210°C as compared with dry granules processed at 240°C (Fig. 1).

Rheological Changes

The changes in the melt viscosity for unextruded granular PLLA material by time of measurement in the DMTA equipment are shown in Figure 3. For the dry material, the initial melt viscosity was dependent on the temperature used and the

decrease in melt viscosity by time increased by increasing temperature. The initial melt viscosity both at 210 and 225°C is lower in case of conditioned granules than for the dry specimen. The rate of decrease in melt viscosity is higher for the conditioned granules than the dry specimen, which shows that the presence of moisture in the polymer increases the degradation rate at 210 and 225°C. The melt viscosity measured at 240°C is independent of the moisture content in the granules.

The melt viscosity measured at 240°C at the time interval corresponding to the residence time of the melt in the extruder at 20 rpm is very low. This measured viscosity is too low for regular melt processing equipment. This was also observed in our extrusion experiments where the low torque at 240°C and 20 rpm was accompanied by very low viscosity of the molten polymer.
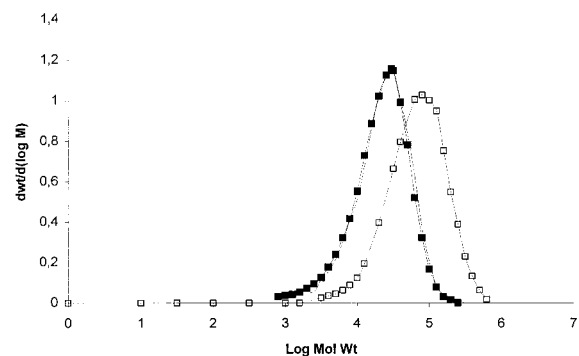
A.
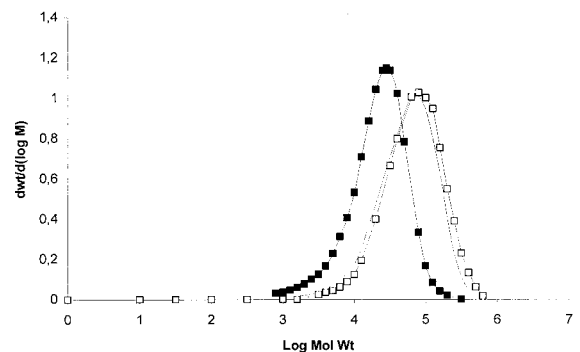
B.

Figure 2   Size exclusion chromatograms. (A) Untreated (—□—), 210°C, 20 rpm, 0% RH (—), 210°C, 20 rpm, 65% RH (—■—). (B) Untreated (—□—), 240°C, 20 rpm, 0% RH (——) 210°C, 20 rpm, 65% RH (—■—).
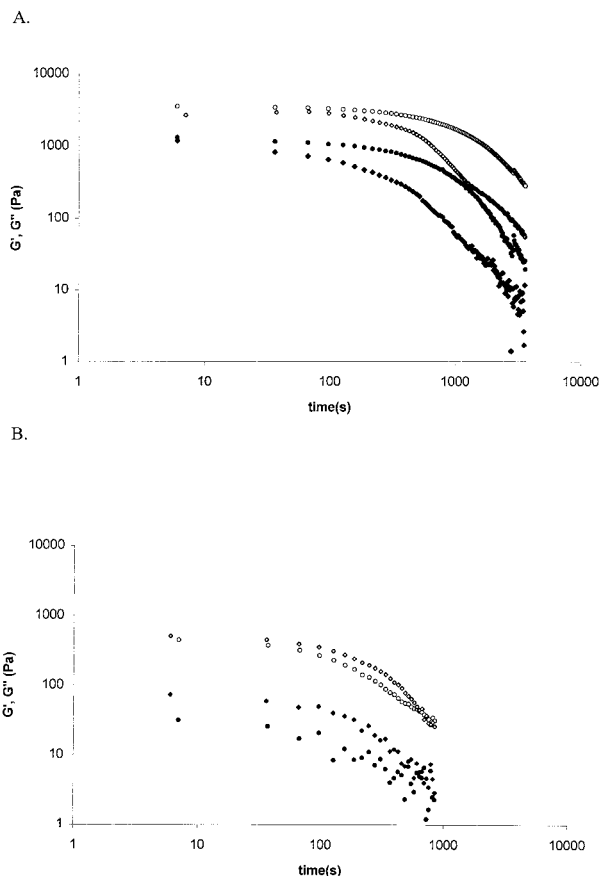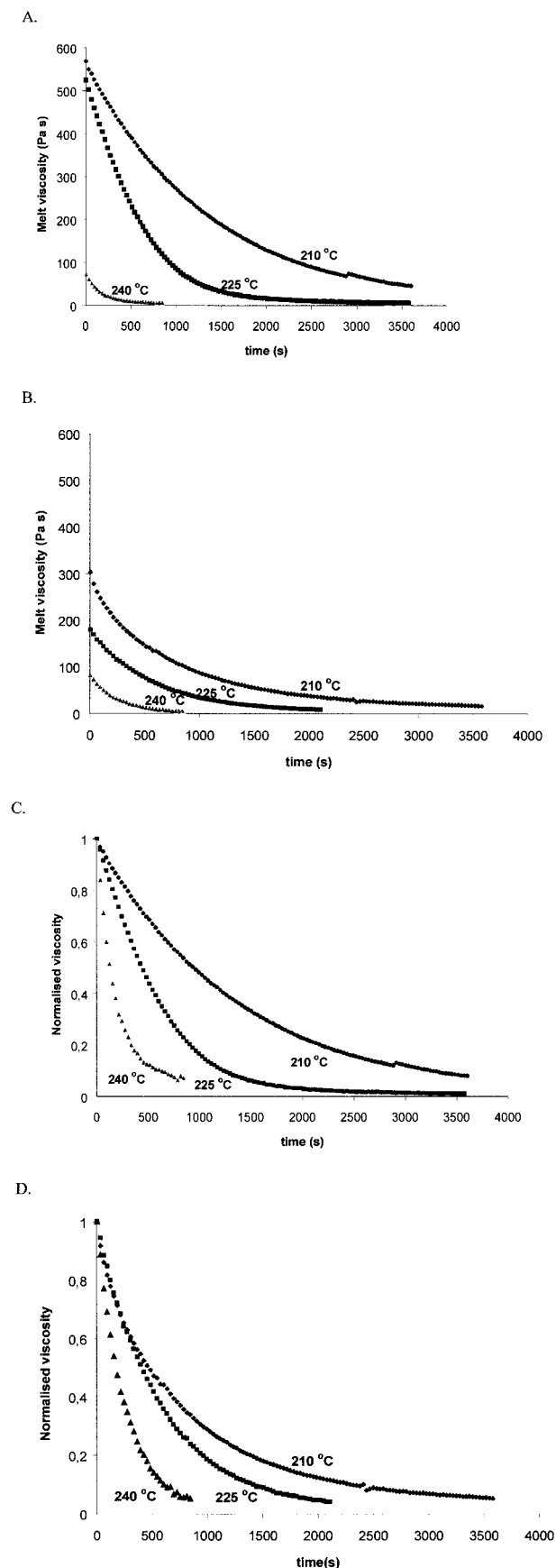
A.

B.

C.

D.

A.

B.

Figure 4   Storage modulus, G^I, and loss modulus, G^{II}, as function of time at (A) 210°C and (B) 240°C. ■, G^I dry samples; ○, G^{II} dry samples; ▲ G^I samples conditioned at 65% RH prior to measurements; △, G^{II} samples conditioned at 65% RH prior to measurements.

Shear and loss modulus, G^I and G^{II}, as functions of time, are shown in Figure 4. At 210°C, It is observed for conditioned specimens that the loss in G^I and G^{II} starts earlier and is faster as compared with the dry samples. At 225 and 240°C, the values of G^I and G^{II} are lower compared to G^I and G^{II} measured at 210°C and the decrease in G^I and G^{II} starts after short times of measurement; beyond 100 s, these values cannot be measured with good accuracy.

The correlation between molecular weight measured by SEC and MFI was studied. No correction has been given to eventual degradation of

Figure 3   Melt viscosity (η) as function of processing time at 210, 225, and 240°C for (A) dried and (B) conditioned samples. In (C) and (D) the normalized curves are shown.
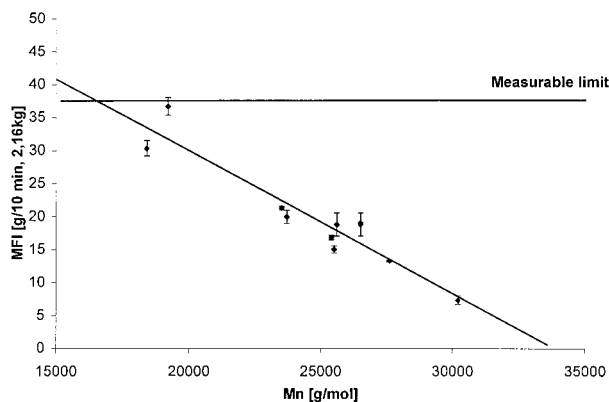
Figure 5 Melt Flow Index (MFI) as a function of molecular weight measured as M_n.

the polymer during the measurements or by differences in the moisture content prior to measurement. An inverse linear correlation was shown to exist between MFI and M_n (Fig. 5) or MFI and M_w. The reason for the linear relationship is probably due to the small differences in MWD for the different samples. For the samples with M_n below 15,000 g/mol, the MFI could not be measured due to the low melt viscosity. From Figure 5 it can be stated that MFI measurements could be a rapid and useful method for analysis of the molecular weight of PLLA samples in the molecular weight region investigated.

Mechanical Properties

The stress at break for the specimens varied from 31.8 to 61.8 MPa and the corresponding strain at break from 1.5 to 3.5%, depending on the processing conditions used (Fig. 6). For the dry granules extruded at 210°C and 120 rpm, the stress at break was 61.8 MPa and strain at break 3.5%. For dry samples processed at 210°C and 20 rpm, the stress at break was 58.5 MPa and strain at break 2.6%. For dry samples processed at 240°C, the stress at break was 54.5 and 35.6 MPa, strain at break 3.2 and 1.7% for 120 and 20 rpm, respectively.

For the conditioned granules extruded at 210°C, a decrease in stress and strain at break was observed compared to the dry granules for both 20 and 120 rpm. The difference in stress and strain at break between the conditioned granules processed at 20 or 120 rpm were also large compared to the dry granules (Fig. 6). When processed at 240°C at 20 and 120 rpm, the effect of conditioning the granules prior to extrusion on

the tensile properties was not as significant as at 210°C. It is probably due to the greater degradation at 240°C, compared with 210°C, which as reported previously was observed in the melt viscosity and molecular weight measurements.

The correlation between M_n, in the range of 10,000 and 35,000 g/mol, and stress at break are shown in Figure 7. It can be seen that the stress at break increases with increasing molecular weight, especially in the region of 10,000 to 20,000 g/mol. The critical chain length (i.e., the minimum chain length to obtain chain entanglements in the material) has been reported to be within the range of 16,000 to 21,000 g/mol for PLLA polymer.[21,22] The chain entanglements influence properties such as melt rheology and solid mechanical properties.[23] It could be a probable explanation for the faster decrease in stress at break for the samples with M_n below 20,000 g/mol used in this work.

Earlier reports[24] have shown that there are no correlation between stress at break and molecular weight for noncrystalline PLLA samples. In our case, there is an obvious difference in mechanical properties between samples extruded at different conditions. In order to exclude differences in crystallinity as the main reason for different mechanical properties, the crystallinity was determined by DSC. The degree of crystallinity for the different samples in the present studies varied in the range of 16–20% except for the conditioned granules processed at 240°C and 20 rpm, which showed a crystallinity of 9%. It can thus be concluded that differences in mechanical properties of PLLA are not due to differences in crystallinity.

CONCLUSION

In the processing of the PLLA material used, it is demonstrated that the temperature in the extruder must be kept at a low level to minimize degradation of the polymer during processing. At the lowest processing temperature used, 210°C, the loss in M_n is less dependent on the residence time in the melt compared to when processed at a temperature of 240°C. The presence of moisture in the material affects the loss in M_n to a great extent when processing is done at 210°C. Processing of PLLA at 240°C and 20 rpm results in severe thermal degradation and the moisture content in the polymer probably does not contribute further to the degradation process.
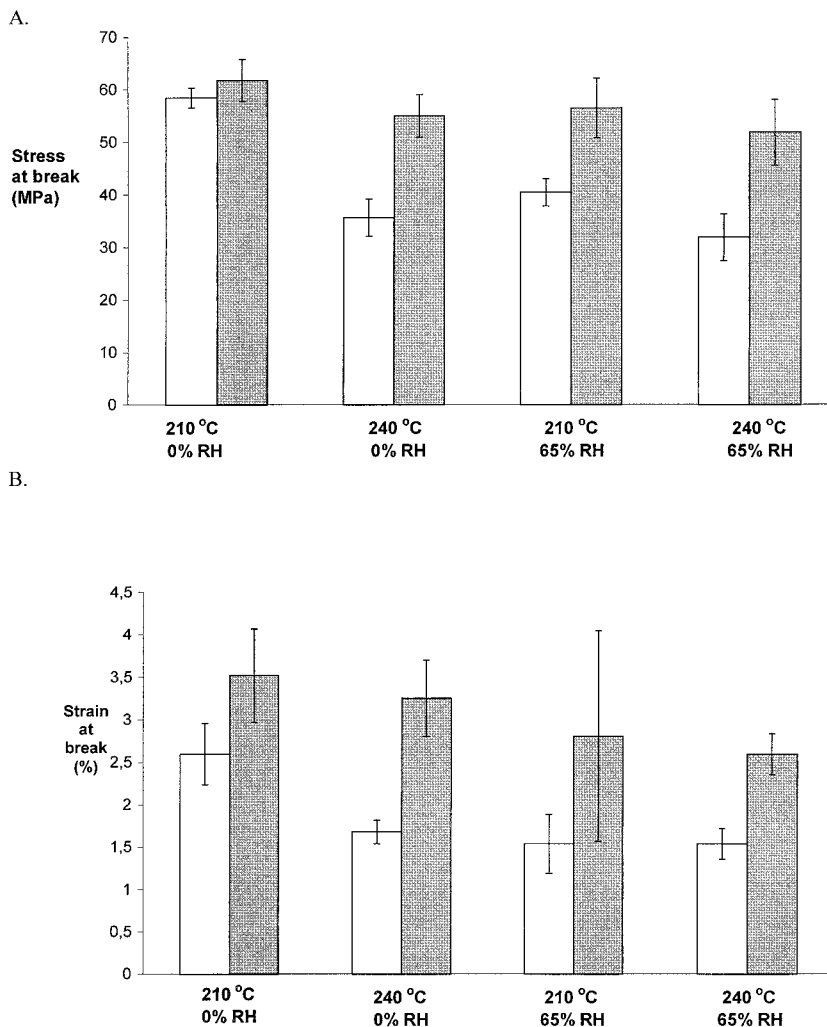
A.

B.

Figure 6 (A) Stress and (B) strain at break at different processing conditions. White, 20 rpm; gray, 120 rpm.

The stress and strain at break decreases when the molecular weight of PLLA decreases. At molecular weights below 20,000 g/mol, the rate 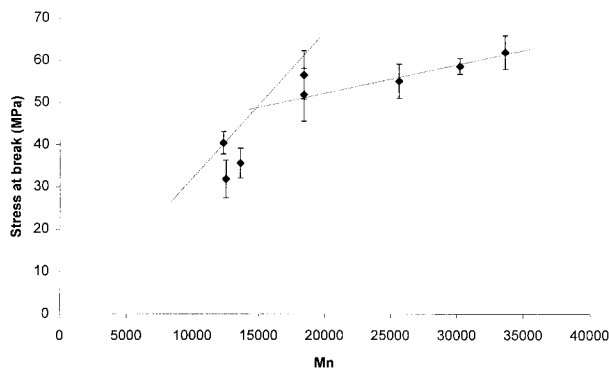of decrease is greater compared to higher molecular weights. This can be attributed to very short chain lengths, which also results in decreasing the number of chain entanglements necessary to hold the molecular structure intact.

Figure 7 The stress at break as function of M_n.

REFERENCES

1. Bendix, D. Polym Degrad Stab 1998, 59, 123–135.
2. Vert, M.; Christel, P.; Garreau, H.; Audion, M.; Chanavaz, M and Chabot, F. Totally bioresorbable composites systems for internal fixation of bone fractures. In Polymer Science and Technology 34.

International Conference on Polymers in Medicine: Biomedical and Pharmaceutical Applications. Chellini, E.; Giusti, P.; Migliaresi, C.; Nicolais, L., Eds., Capri, Italy, 1985, pp. 263–275.

3. Vert, M.; Chabot, F. Makromol Chem Suppl 1981, 30–41.

4. Leenslag, J. W.; Pennings, A. J.; Bos, R. R. M.; Rozema, F. R.; Boering, G. Biomaterials 1987, 8, 311–314.

5. Leenslag, J. W.; Pennings, A. J.; Bos, R. R. M.; Rozema, F. R.; Boering, G. Biomaterials 1987, 8, 311.

6. Winter, G. D.; Gibbons, D. F.; Plenk, H. Biomaterials 1980.

7. Schlicht; R. Kunststoffe 1998, 88, 880–889.

8. Chang, B.-H. Polym News 1997, 22, 307–313.

9. Meinander, K.; Niemi, M.; Hakola, J. S.; Selin, J.-F. Macromol Symp 1997, 123, 147–143.

10. Sinclair, R. G. J Macromol Sci, Pure Appl Chem 1996, A33, 585.

11. Spruiell, J. E. INDA-TEC 97; INDA, Association of the Nonwoven Fabrics Industry, 25.0, 1997.

12. Jamshidi, K.; Hyon, S. H.; Ikada, Y. Polymer 1988, 29, 2229.

13. Gogolewski, S.; Jovanovic, M.; Perren, S. M.; Dillon, J. G.; Hughes, M. K. Polym Degrad Stab 1993, 40, 313.

14. VanOepen, R.; Michaeli, W. Clin Mater 1992, 10, 21.

15. McNeill, I. C.; Leiper, H. A. Polym Degrad Stab 1985, 11, 267.

16. McNeill, I. C.; Leiper, H. A. Polym Degrad Stab 1985, 11, 309.

17. Garrozzo, D.; Guffrida, M.; Montando, G. Polym Bull 1986, 15, 353.

18. Södergård, A.; Näsman, J. H. Polym Degrad Stab 1994, 46, 25–30.

19. Fisher, E. W.; Stergel, H. J.; Wegner, G. Kolloid ZZ Polym 1973, 251, 980.

20. Grijpma, D. W.; Penning, J. P.; Pennings, A. J. Colloid Polym Sci 1994, 272, 1068–1081.

21. Cooper-White, J. J.; Mackay, M. E. J Polym Sci, Part B: Polym Phys 1999, 37, 1803–1814.

22. Wu, S. J. J Polym Sci, Part B: Polym Phys 1989, 27, 723–741.

23. Perego, G.; Cella, G. D.; Bastioli, C. J Appl Polym Sci 1996, 59, 37–43.

24. Södergård, A. PhD Thesis; Åbo Akademi, Åbo, 1996.