

Effect of Processing Parameters on Microstructure and Tensile Properties of PLLA Using Micro-Injection Molding

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Abstract

Using micro-injection molding as a processing method, the effect of injection speed and mold temperature on the in-mold crystallization of poly(L-lactic acid) (PLLA) is investigated. Test bars were micro-molded at injection speeds of 50 mm/s up to 600 mm/s, keeping the mold cavity temperature during filling at 30 and 100 °C. Differential scanning calorimetry and wide angle X-ray diffraction were used to assess the structure development during processing. Tensile tests were also carried out to determine the elastic modulus as a function of the molding conditions.

Introduction

Poly(L-lactide) (PLLA) is a thermoplastic obtainable from renewable resources which has found usage in packaging as well as in medical applications such as bioresorbable sutures for healing wounds and plates and screws for craniofacial surgery. PLLA can be melt processed but careful conditions should be observed to avoid hydrolytic degradation above the glass transition temperature (50 to 60 °C) as well as depolymerization above 230 °C (1). It has also been shown that high shear stresses during melt processing can have an effect on the crystallization kinetics of PLLA (2). This last aspect has not been studied extensively however and it is the purpose of this work to investigate the effect processing parameters on crystallization of PLLA using the injection molding process. The final crystalline content of melt processed PLLA is also dependent on the thermal history during the shaping process. It is therefore our purpose to concentrate on the effect of injection speed which will impose the extent of shearing and also on the effect of mold temperature during the filling and solidification stages.

Experimental

Tensile testing bars with dimension shown in Figure 1 were molded in a Battenfeld Microsystem 50 microinjection molding machine. This micromolding press was chosen because of the small polymer quantities which are needed and the possibility to use high injection speeds along with a good control of the mold temperature. The molding tests were carried out using poly(L-lactide) acid, PLLA Biomer 9000, supplied by Biomer (Germany). DSC tests carried out on virgin material revealed a glass transition temperature of about 58°C and small melting peak at 169°C. This grade is basically amorphous but crystallization can occur during molding, depending on the cooling conditions. The melt temperature at the nozzle was

set at 200 °C as recommended. In a first series of molding the mold temperature was set at 30°C for the whole cycle. In a second series of experiments, the mold was heated up to 100°C prior to filling, maintained to that temperature during holding (600 bars during 5 s), then quickly cooled to about 30°C. The injection speed for both series of tests was varied from 50 to 600 mm/s.

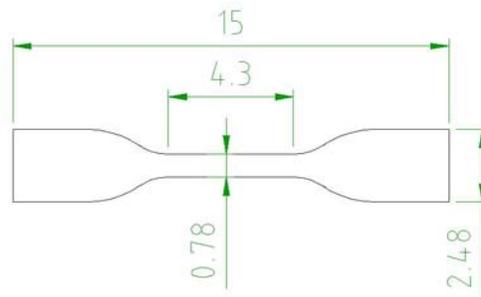


Figure 1 – Micro test bar dimensions, mm.

Wide angle X-ray diffraction (WAXD) was performed on the central zone between the two necks of the molded samples using the Bruker D8 Advance x-ray diffractometer. Differential scanning calorimetry (DSC) tests were also run on samples weighing about 5 mg taken in the same location as the WAXD technique. Both methods were used to assess the change in crystallinity due to the effect of the molding conditions. Finally, a tensile microtester model 5548 from Instron equipped with a 2kN load cell was used to measure the room temperature elastic modulus in relation to the molding conditions. A traction speed of 5 mm/min was used for all the tests.

Results and Discussion

The as molded testing bars were all visually perfectly clear and transparent which might indicate that the material, upon solidification in the mold, remained mostly in the amorphous state. This is basically confirmed by the WAXD results as shown in Figure 2. The sample molded at the highest injection speed of 600 mm/s in a cold mold (30 °C) has no crystallinity whatsoever: the corresponding x-ray diffraction pattern shows a broad amorphous peak. On the other hand, the samples molded at a mold temperature of 100 °C display x-ray diffraction patterns with sharp peaks, typical of a crystalline phase, at an angle 2θ of 16.3° on top of the broad amorphous peak. The degree of crystallinity, calculated as the percentage of the scattered intensity of the crystalline phase over the total scattered intensity, was found to be quite small, with the sample obtained at the slowest injection speed having the largest crystalline content. The DSC results for the as molded samples are presented in Figure 3. The heating scan started from 30 °C up to 210 °C at a heating rate of 10 °C/min. The samples were maintained at that temperature for 5 min before being cooled back to 30 °C at the same rate. All the samples show a broad exothermic peak due to crystallization in the vicinity of 114 °C for all the samples with the exception of the sample injected at the slowest injection speed which saw a shift in the crystallisation peak at 123 °C. For all four samples the endothermic peak of fusion was at 169°C whereas the glass transition temperature is similar to the one obtained with virgin material and is about 59 °C.

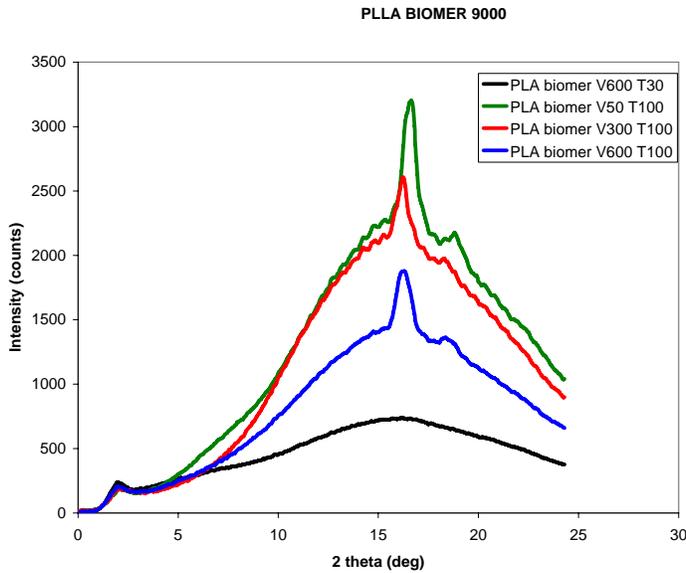


Figure 2: X-ray diffraction patterns of as-molded samples

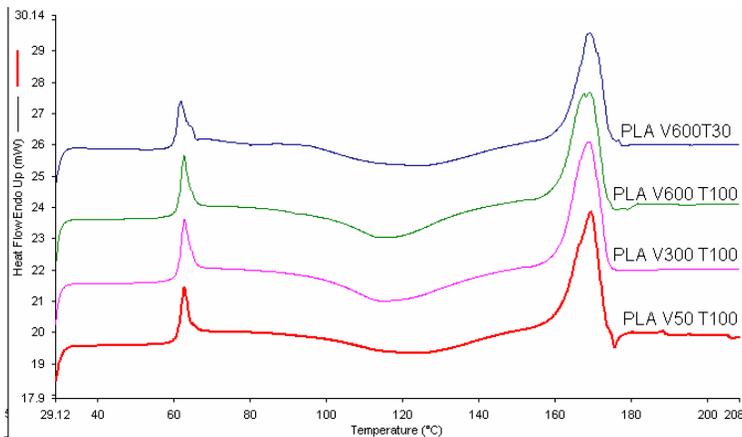


Figure 3: DSC diagram of as molded PLLA samples

To calculate the degree of crystallinity, the difference in heat flow per unit mass during fusion and crystallization was divided by 93 J/g, the enthalpy of fusion of pure crystalline PLLA as reported in (3). The results are shown in Table 1 along with the degrees of crystallinity derived from WAXD. We first note that, for all samples, the degree of crystallinity obtained by DSC (X_D) is still low (less than 12%) but at least three times higher than the degree of crystallinity obtained by WAXD (X_W). With both methods the intermediate injection speed resulted in the lowest crystalline content. The table also gives the elastic moduli as obtained by the tensile tests. If we compare the samples molded in the hot mold, it is clear the highest injection speed resulted in the largest modulus. If a higher crystalline content correlates with a high strength, then this result is in agreement with the DSC results. Also, for the same injection speed, the sample molded at a higher mold temperature during filling displayed a higher strength.

Table 1

Samples	V50 T100	V300 T100	V600 T100	V600 T30
X_W	3.0	1.2	2.0	-
X_D	9.8	5.6	11.4	11.0
E, MPa	1552	1464	1900	1500

Conclusion

A preliminary study was conducted on the effect of the micro-injection molding process parameters (injection speed and mold temperature during filling) on the microstructure development of poly(L-lactide) acid through the evaluation of the crystalline content of the molded samples. For all conditions used the crystallinity content was low but more sensitive to the mold temperature than to the injection speed. This is better seen from the mechanical tensile tests. There is a marked difference between the degree of crystallinity determined by WAXD and DSC which needs to be investigated.

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