



## Effects of ultrasonic vibration on the micro-molding processing of polylactide



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### ABSTRACT

A new ultrasonic micro-molding system was used to process polylactide (PLA) and fabricate reduced dimension specimens. Plasticization and molding of PLA were achieved by applying ultrasonic waves after feeding the polymer into a plasticizing chamber. Chemical and physical characteristics of processed PLA varied depending on the processing window (i.e. changes in ultrasonic wave amplitude between 14.2 and 48.1  $\mu\text{m}$  and molding pressure between 0.5 in 6 bars). In terms of chemical effects, the application of ultrasound can lead to lower molecular weights (e.g. decreases of more than 45% in the weight average molecular weight), revealing partial degradation of the material. Also, the processed materials exhibited slightly higher thermal degradability than pure PLA because ultrasonic vibrations break molecular linkages and worsen the polymer structure. Finally, the processing conditions for the preparation of PLA specimens could be optimized without causing degradation and preserving structural characteristics and mechanical properties. Specifically, the use of an amplitude of 48.1  $\mu\text{m}$  and a pressure of 3 bars gave samples with the same molecular weight as the raw material (i.e. 117,500 g/mol as opposed to 117,300 g/mol for  $M_w$ ).

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### 1. Introduction

Injection molding is one of the most popular large scale polymer processing methods due to its high productivity and flexibility [1]. However, the use of this technique to obtain single micro parts in fields like electronics, medicine or biotechnology is quite disadvantageous. The main problem lies in the low dosage precision, which results in a large amount of material being rejected during injection. Very often over 90% of the polymer is wasted and this can be an important cost factor, especially in the case of polymers used for advanced applications [2]. Another disadvantage of micro-injection molding is that filling the mold can be rather complex due to the frozen layer appearing near the mold surface [3]. Moreover, in many cases injection molding methods involve high temperatures, long heating times and mechanical stresses which can contribute to polymer degradation. In fact, the literature reports large variations in the molecular weight of some temperature sensitive polymers, such as polyesters. For instance, Witzke [4], Perego et al. [5] and Gogolewski et al. [6] reported molecular weight losses of 5–52%, 50–88%, and 14–40%, respectively, for injection molded polylactide (PLA).

Various heating techniques based on high frequency radiation [7,8] have been developed in order to reduce cycle time and prevent polymer chain scission. Despite providing fast heating of the mold surface, these techniques are still quite time consuming.

Recently, ultrasonic waves have been used for fabricating micro parts from thermoplastic polymers due to the capability of energetic ultrasound to heat and deform materials cyclically at ultrasonic frequencies, thus providing a more energy-efficient solution. Nevertheless, the potential applications of ultrasonic technology in the field of micro-injection molding are still limited despite some advantages over conventional injection molding [9]. This technology has been applied to fabricate micro-fluidic components by micro-scale ultrasonic welding [10], improve microstructures in weld-line areas [11] or fabricate micro-features on polymer substrates [12,13]. However, up to now very few reports describe plasticization of polymers by an ultrasonic source together with direct injection of molten material to obtain reduced size samples in a single step [2,9,14]. This procedure also offers the possibility of delivering just a small amount of molten material, just as required in a micro-molding process, to ensure dosage precision.

The application of an ultrasonic field to a polymer melt has proved to significantly reduce viscosity due to a combination of physical and chemical factors [15,16]. Regarding the former, the vibration disturbs the convergent melt flow in the entry region

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while reducing elastic tensile strains. Moreover, the ultrasonic energy reduces molecular chain entanglement and facilitates molten polymer flow [17]. On the other hand, the major chemical effects of ultrasound are due to cavitation, which implies nucleation, growth, and claps of bubbles or cavities, resulting in violent shock waves [18]. The sound waves that propagate into the molten material bring about alternating high-pressure (compression) and low-pressure (rarefaction) cycles. This phenomenon leads to rapid growth of the weak sites of the molten material, which predominantly contain dissolved gases (cavitation nuclei), giving rise to vapor-filled and gas-filled cavities or microbubbles [19,20]. Alternatively, some authors have suggested that chain breakages can be caused by a temperature increase induced by ultrasonic waves [15,16]. However, the capability of ultrasonic irradiation to induce polymerization reactions has also been reported [21].

To date, few reports have explored the influence of ultrasound on structural characteristics and final properties of specimens prepared by ultrasonic plasticization. Specifically, they deal with polyaddition commodity polymers such as polypropylene, polyethylene or polystyrene [15,17]. Nevertheless, the effect of combining ultrasound with direct injection to plasticize material on structural characteristics, morphology and final properties of specimens has not yet been explored. It is clearly necessary to set up opportunities or limitations of this new processing technique due to its potential with polymers used in fields such as biomedicine, biotechnology or electronics, or even in the characterization and development of new synthetic polymers only available in small laboratory scale.

In the present study, a new ultrasonic micro-molding apparatus is employed to process polylactide (PLA) and fabricate reduced size specimens. PLA is currently one of the most widely used biomaterials due to its good physical properties and biocompatibility. Furthermore, PLA has relatively low thermal and hydrolytic stability, which can be useful in exploring and extrapolating the applicability of the new technique for this class of polymers. Specifically, the influence of ultrasonic waves on PLA structure, degradation and mechanical properties is established. Finally, the feasibility of preparing PLA specimens with retention of overall properties is explored.

## 2. Experimental

### 2.1. Materials

The polylactide (PLA) used in this study is a commercial product (PLA Polymer 3051D) of NatureWorks® (U.S.A) characterized by a melt flow index of 10–25 g/10 min (measured at 210 °C with 2.16 kg according to the D-1238 standard). The polymer was stored under vacuum before use.

### 2.2. Micro-injection processing equipment

A prototype ultrasound molding machine (Sonorus® fabricated by Ultrason S.L.) was used. The apparatus is based on a controller, a transducer, a pneumatic pressure system, a thermally controlled mold and an acoustic unit, as schematically shown in Fig. 1a. The controller (1000 W - 30 kHz digital ultrasound generator from Mecasonic fitted with a 3010 DG digital system) regulates the oscillation time, molding pressure and amplitude of the ultrasonic wave. The transducer (Mecasonic) converts electrical energy into kinetic energy and creates undulatory movement. The pneumatic pressure system (Ultrason S.L.) applies a constant molding pressure (0–6 bar) to the material while ultrasound is generated by the sonotrode tip. Thermally controlled molds (Ascamm) are

designed to prepare eight test specimens of small dimensions, or alternatively, pieces with high precision details. The acoustic unit (Mecasonic) mainly consists of a booster and a sonotrode. The first element amplifies or reduces the wave amplitude (0–137.5 μm) while the second transfers vibration energy to the material and provides the pressure required to transfer it into the mold. The amount of vibration energy generated depends on the amplitude level. Vibration helps to control the amount of energy supplied by the system to the polymer for it to melt and reach the flow properties required for cavity filling.

In terms of operational steps, solid material is fed and ultrasound is transmitted from the sonotrode to the polymer in a plasticizing chamber. The material flows through the feeding channels and fills the mold. The feeding channels filled with molten polymer work as a resonance box that facilitates the molding process. The mold can also contain a thermal controller to record temperature variation during the micro-molding process.

### 2.3. Micro-molding experiments

PLA was processed by ultrasonic micro-molding under the conditions in Table 1. Ultrasonic waves were applied after the cavity was filled with polymer pellets. The dimensions of the tensile test specimens were 1.5 × 0.1 × 0.1 cm<sup>3</sup> under IRAM-IAS-U500-102/3 standards.

### 2.4. Measurements

Molecular weight was estimated by size exclusion chromatography (SEC) using a liquid chromatography equipment (Shimadzu, model LC-8A) provided with an Empower computer program (Waters). A PL HFIP gel column (Polymer Lab) and a refractive index detector (Shimadzu RID-10A) were employed. The polymer was dissolved and eluted in 1,1,1,3,3,3-hexafluoroisopropanol containing CF<sub>3</sub>COONa (0.05 M) at a flow rate of 0.5 mL/min (injected volume 100 μL, sample concentration 1.5 mg/mL). The number and weight average molecular weights and molar-mass dispersities were calculated from two specimens and using polymethyl methacrylate standards.

Thermal degradation was studied at a heating rate of 2 °C/min with around 5 mg samples in a Q50 thermogravimetric analyzer of TA Instruments and under a flow of dry nitrogen. Test temperatures ranged from 50 to 600 °C.

Calorimetric data were obtained by differential scanning calorimetry with a TA Instruments Q100 series equipped with a refrigerated cooling system (RCS). Experiments were conducted under a flow of dry nitrogen with a sample weight of approximately 5 mg, while calibration was performed with indium. PLA polymer samples were analyzed using a heating scan (20 °C/min) from 20 to 200 °C. In some cases, a second heating run was performed with samples previously cooled from the melt state at a low rate (10 °C/min).

Infrared absorption spectra were recorded in the 3600–600 cm<sup>-1</sup> range with a FTIR 4100 Fourier Transform spectrometer from Jasco. A MKII Golden Gate attenuated total reflection (ATR) accessory from Specac was employed.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were acquired with a Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz, respectively. Chemical shifts were calibrated using tetramethylsilane as an internal standard. Deuterated chloroform (CDCl<sub>3</sub>) was used as the solvent at room temperature.

Inspection of the morphology of pure PLA and the corresponding processed samples was conducted by scanning electron microscopy using a Focus Ion Beam Zeiss Neon 40 instrument (Carl Zeiss, Germany). Carbon coating was accomplished by using a

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