In vitro Degradation Study of Poly(L-lactide)-Based Fibers using Dynamic Mechanical Analysis

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Statement of purpose: Dynamic Mechanical Analysis (DMA) is a widely used non-destructive technique for characterization of viscoelastic properties of synthetic materials. The degree of relaxation of polymeric materials at room or body temperature plays an essential role in the development of novel biodegradable surgical articles (sutures, staples, wires) [1,2].

In this communication, four types of poly(L-lactide)-based resins were synthesized, melt-extruded into fibers, and their *in vitro* degradation at 37 °C evaluated. Specimens were analyzed by DMA under constant tension before and after *in vitro* degradation. The time-temperature superposition (TTS) principle was applied for evaluation of material long-term properties. Results indicate that DMA-TTS can be an efficient approach for screening stress-relaxation phenomena in biodegradable polymers and can provide information on the implication of the viscoelasticity on surgical outcome[1].

Methods: Biodegradable resins were synthesized and melt extruded according previously disclosed procedure[3]. DMA analyses were performed using a DMA Q800 (TA Instruments) with Tension Film/Fiber Clamp. All fibers had a diameter = 0.5 mm and length = 150 mm. Other test parameters included: strain amplitude = 20 µm; pre-load force = 0.01 N; temperature ramp = -50 °C to 150 °C with 5 °C steps; frequency sweep = 0.1 to 10 Hz. The TTS shift was performed at a reference temperature of 20 °C. Percentage of strength retention *in vitro* was evaluated by tensile testing using an Instron Model 5543.

Results: Four types of block copolymer resins: LP1, LP2, LT1, and LT2 [L = (L)-lactide, P = p-dioxanone, T = trimethylenecarbonate] were studied. Figure 1.a. shows tensile storage modulus of the fibers as a function of temperature and frequency. All specimens exhibited a number of transitions: α, β, and melting. While commercially available sutures DS1, DS2 (degradable) and ND (non-degradable) start losing their stiffness at room temperature, the newly synthesized fibers retain high degree of stiffness up to 60-70 °C. The TTS principal was applied to multifrequency experiments to obtain master curves (Figure 1.b.). These results indicate that the fibers from newly synthesized resins retain a high degree of stiffness over a long period of time at room temperature. A similar trend has been reported for silk sutures which are known as the standard of performance[2,4]. *In vitro,* the change in strength was related to the chemical structure of the resin with LP1 and LP2 being more prone to degradation than LT1 and LT2 (Figure 2). TTS master curves of the samples after *in vitro* degradation (Figure 3) showed complex changes in fiber properties namely, a slight decrease in the modulus due to degradation and an increase in propensity for brittleness over a long period of time due to the induced crystallization as reported by Fu et al.[5]

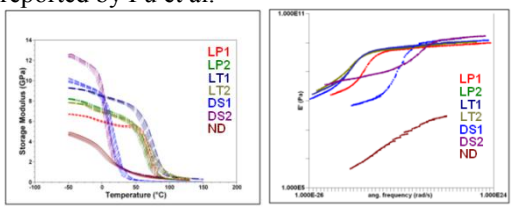

Fig.1. a. Stepwise isothermal frequency sweep of PLA-based fibers (LP1, LP2, LT1, LT2) and commercially-available sutures (DS1, DS2, ND). b. TTS master curves for PLA-based fibers and commercially-available sutures.

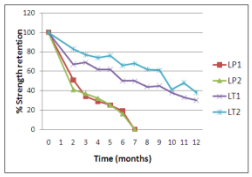

Fig. 2. Strength retention (%) of LP1, LP2, LT1, and LT2 subjected to *in vitro* degradation at 37 °C for 12 months.

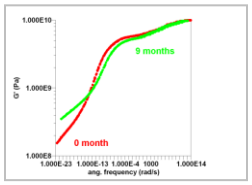

Fig. 3. TTS master curves for LT2 (see Fig.1) at 0 (red) and 9 (green) months *in vitro* at 37 °C.

Conclusions: Viscoelastic properties of poly(L-lactide)-based fibers were determined using DMA analysis with TTS. The synthesized fibers were found to retain a higher degree of stiffness over a long period of time at room temperature. DMA testing of degradable fibers subjected to *in vitro* degradation demonstrated their susceptibility to induced crystallization.

References:

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