Molecular Modulation of Long Lasting Absorbable Polymers for Compliance and Selective Degradation

J.A. Lilley, K.D. Gray, M.S. Taylor
Poly-Med, Inc., Anderson, SC

Statement of Purpose:

Long lasting absorbable polymers made of poly l-lactide (PL) and poly-(ε-caprolactone) offer good strength retention characteristics, maintaining up to 88% of its initial tensile after 3 months *in vivo*[1], and have been used in numerous medical devices. However, PL has relatively high modulus of 2 GPa[2] in injection molded parts and PCL, while less stiff, is known to creep at body temperature, both of which limit their applications. Co-polymerization of these two materials offers opportunities to combine favorable characteristics of both for incorporation into new types of devices. Additionally, the way which the chains are bonded could allow tuning of resultant polymer properties thereby creating a means of modulation without chaining the overall degradation byproducts.

Methods:

Polymers were created with 75 wt% l-lactide, 25 wt% ε-caprolactone in diblock (DI), triblock (TRI), and random (RAND) configurations by changing initiator and reaction conditions with the same M/I ratio to generate equivalent chain lengths. After drying, all copolymers were injection molded in an Arburg Allrounder 270C, 33 ton injection molding machine at 210°C and 10ccm/s injection flow into Type V tensile bars, along with homopolymer PL (Purac) and PCL (Dow Chemical). Mechanical tests were conducted on a MTS Synergie 2000 screw-actuated tester. Tensile tests were conducted with 2.55 cm grip spacing at a test speed of 100 mm/min. Static 3-point bend tests were conducted on a 2.00 cm span with 0.63 mm diameter rollers and test speed of 50 mm/min using a strain end point of 15%. Samples were placed *in vitro* at 37°C and 7.4 pH buffered saline solution and removed periodically over 12 weeks to study retention properties.

Results:

As expected, PLA exhibited the highest modulus response in both flexion and tension test modes (Figures 1 and 2). Both tensile and bending moduli were reduced with the introduction of caprolactone into the polymer chain. In both cases, the diblock configuration has a higher modulus than the triblock. Random and diblock configurations demonstrate significate loss of strength over time while the triblock structure retains strength similar to the neat materials over time. In general, the polymer structure defines the potential for formation of crystalline and amorphous segments, which modulates the resulting mechanical and *in vitro* performance of the molded articles.

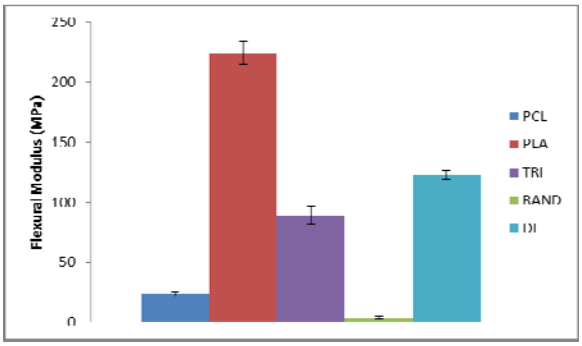

Figure 1: Flexural modulus of injection molded materials.

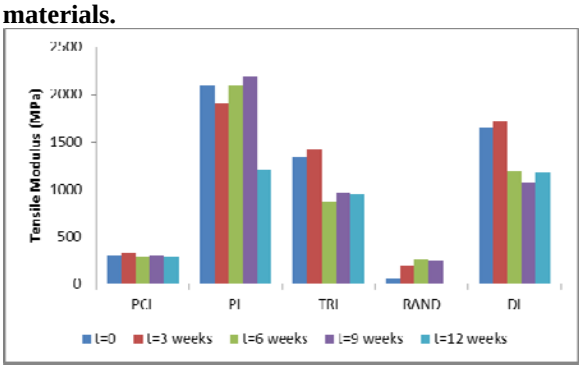

Figure 2: Tensile modulus reduction for 12 weeks at 37C, 7.4 pH.

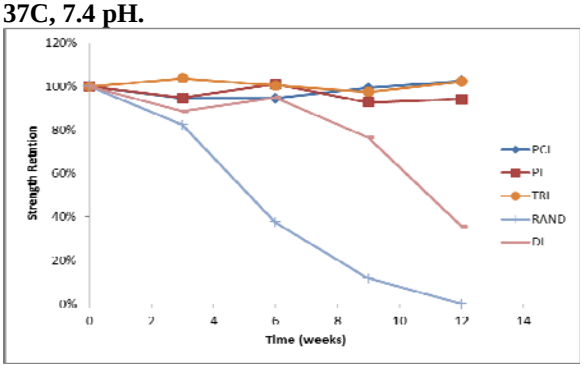

Figure 3: Tensile strength retention for 12 weeks at 37C, 7.4 pH

Conclusion: Even with the same composition, polymers can exhibit significantly different mechanical and degradation responses, illustrating the need to design the proper polymer for the application. Initial mechanical results demonstrate promise for developing flexible polymers for long lasting medical applications. To completely evaluate these materials for suitability in implant-specific applications more mechanical tests, such as fatigue and creep, need to occur..

References:

1. Krishna, C et al., *Journal of Biomaterials Applications*, 25, 321 (2010).
2. Ghosh, s. et al., *Polymer Engineering and Science*, 47, 1147 (2007).