Issues in Fabrication and 3D Printing of Tissue Engineering Scaffolds from degradable polymers

N. Sanjeeva Murthy and Joachim Kohn

New Jersey Center for Biomaterials, Rutgers, The State University, Piscataway, NJ 08854

Statement of Purpose
Degradability that makes a large class of polymers attractive in many biomedical applications also makes it difficult to process them. The most widely used 3D printing techniques, Fusion Deposition Modeling (FDM), gets around this problem by heating the polymer filament for a short duration prior to printing. But the problem does not disappear because the filaments need to be extruded. We investigated the interactions among the key processing parameters, temperature, moisture content, shear rate and residence time, which influence the kinetics of degradation, crosslinking and the evolution of gaseous byproducts.

Materials and Methods
Three family of polymers, polylactides, and tyrosine-derived polycarbonates and poly(ester amides) were investigated [1]. Melt rheology measurements were carried out on Rosand capillary rheometer (Malvern Instruments Ltd., UK). Thermal transitions were monitored using differential thermal analysis (DSC) and water and other volatiles were evaluated using thermogravimetric analysis (TGA) (Mettler-Toledo, U.S.A.). GPC (Waters Corporation, MA) was used to monitor the changes in molecular weight.

Results and Discussion
Figure 1 shows the melt viscosity curves of two of the polymers. The data for polylactide shows that the melt viscosity does not change significantly between 180 and 210 °C, and decreases at the onset of degradation at 210 °C. Thus, this polymer can be 3D printed under less-than stringent conditions. In contrast, the viscosity of the polymer labeled E1001(1k), continuously changes with temperature. Such polymers need be processed under stringent conditions

Some of these polymers degrade, i.e., the molecular weight decreases, with time during extrusion (data not shown). This is accompanied by decrease in viscosity of the polymer that makes it difficult to 3D print the polymers to produce reproducible parts. It is also possible that the molecular weight could increase due to thermally induced crosslinking that prevents the polymer from extruded and 3D printed.

Hydration induced degradation in most prevalent in polymers used for biomedical devices, especially in polymers with ester, anhydride and carbonate bonds. Polymers with hydrolyzable bonds are sensitive to
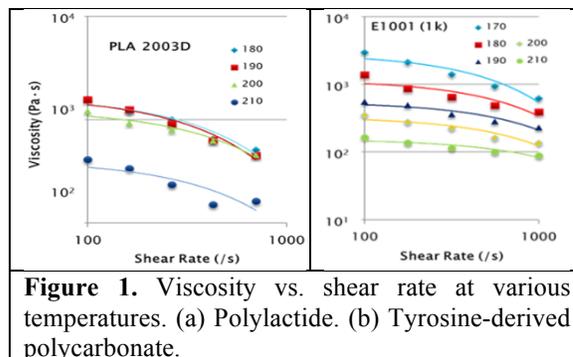

Figure 1. Viscosity vs. shear rate at various temperatures. (a) Polylactide. (b) Tyrosine-derived polycarbonate.

moisture and heat that are invariably present during thermal processing. Figure 2 shows one such mechanism of degradation in a polymer Poly(DTE-*co*-DT-*co*-PEG carbonate). In this polymer, the temperature need to be precisely controlled to prevent the evolution of one of the degradation products CO_2 that was identified using TGA coupled with IR.
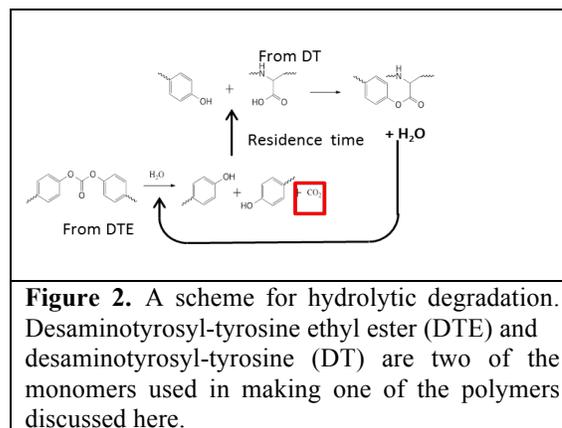

Figure 2. A scheme for hydrolytic degradation. Desaminotyrosyl-tyrosine ethyl ester (DTE) and desaminotyrosyl-tyrosine (DT) are two of the monomers used in making one of the polymers discussed here.

Conclusions
Degradable polymers intended for thermal 3D printing need to be carefully evaluated by thermal and rheological methods, and degradation behavior understood for determining the optimum narrow processing window.

Acknowledgments

References
1. S.L. Burke and J. Kohn, Adv. Drug. Delivery Reviews 92003) 55:447-466.