Biodegradable starch-polyester polymer composites are useful in many applications ranging from numerous packaging end-uses to tissue engineering. However the amount of starch that can form composites with polyesters without significant property deterioration is typically less than 25% because of thermodynamic incompatibility between the two polymers. A reactive extrusion process was developed in which approximately 60% by weight of plasticized starch was blended with a biodegradable polyester (polycaprolactone, PCL) resulting in tough nanocomposite blends with elongational properties approaching that of 100% PCL. During the extrusion process, starch was cross-linked with polycaprolactone in the presence of hydrogen peroxide and montmorillonite (MMT) organoclay, thus compatibilizing the two polymers.

The objectives of this study were to evaluate the mechanical properties of reactively extruded starch-PCL nanocomposite blends, study changes in the morphology of polymer-polymer interface, monitor dispersion of organoclay in the polymer matrix, quantify the effects of reactive extrusion on polymer glass transition, develop a rheological model and scale up the reactive extrusion process from a batch type micro-extruder to continuous twin-screw extruder.
Starch and PCL (36-39 wt% each), glycerol (18-19 wt%), MMT organoclay (3-9 wt%), hydrogen peroxide (0.067 ml/g starch) and ferrous sulfate catalyst (0.0025 g/g starch) were extruded in a co-rotating twin-screw extruder at 120°C and injection molded at 150°C. Elongational properties of reactively extruded starch-PCL nanocomposite blends approached that of 100% PCL at 3 and 6 wt% organoclay. Strength and modulus remained the same as starch-PCL composites prepared from simple physical mixing (non-reactive extrusion). X-ray diffraction results showed mainly intercalated flocculated behavior of clay at 3, 6, and 9 wt% organoclay. Scanning electron microscopy (SEM) showed that there was improved starch-PCL interfacial adhesion in reactively extruded blends than in non-reactive starch-PCL composites. Dynamic mechanical analysis showed changes in primary α-transition temperatures for both the starch and PCL fractions, reflecting cross-linking changes in the nanocomposite blends at different organoclay content. Starch-PCL reactive blends were more pseudoplastic than 100% PCL and showed typical shear-thinning behavior and lower shear viscosities than non-reactive starch-PCL composites. Results from scale-up studies indicated that screw configuration, screw speed and feed rates were important process variables that affected material properties. These were optimized to obtain mechanical properties equivalent to those from the micro-extruder.