Studies on Development of Environmentally Benign Lactone based Polymers and their Composites for Biomedical Applications

Thesis submitted in the partial fulfilment of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

by

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June, 2021

Abstract

The current research work deals with various strategies to chemically connect the monomers (lactide and ε-caprolactone) at the molecular level and reduce the macrophase separation between them which is often witnessed when blending their respective polymers (PLA and PCL). This has been done by the random and block copolymerization techniques, where the block copolymerization (step ring opening polymerization) leads to the improved mechanical properties (strength, elongation, toughness and modulus) with the increasing block length of PLA. The diblock copolymers (PCL-PLA) and their stereocomplex blends are thermally processed by injection molding to form cortical and cancellous bone screws which are further tested for their thermomechanical stability at the sterilization temperature of biomedical devices. The linear triblock copolymers (PLA-PCL-PLA) result in the significant improvement in the mechanical properties as compared to the diblock copolymers. The triblock copolymer is thermally processed by twin-screw extruder to fabricate the filament followed by 3D printing to form a scaffold. The biocompatibility of the block copolymers is ascertained by performing MTT assay using human/rat bone osteosarcoma cells. Preferential formation of stereocomplexation is achieved upon synthesizing stereoblock terpolymers of PLA and PCL. Further, random copolymerization of L-lactide and ε-caprolactone (single step) leads to the development of copolymers which are chemically mixed (giving rise to a single T_g) and varying the content of caproyl and lactyl segments provide the range of materials with variable mechanical properties. Random copolymerization turns out to be an effective strategy for developing thermoresponsive copolymers and/or elastomeric materials. The random copolymer of L-lactide and ε-caprolactone is reinforced with bioglass (upto 50%) by solution casting method. The composites are characterized to determine their mechanical and thermal

properties and are found to behave as near elastomeric materials (with the strain recovery of 500%).

Furthermore, carbon dioxide (CO_2) is used along with 1,3-butadiene gas to develop a precursor (δ-lactone) via high pressure reaction. The use of highly reactive acid such as trifluoromethanesulfonic acid has been made to achieve the cationic polymerization of the metastable monomer. The use of metal catalyst such as Grubb's II generation catalyst in achieving the metathesis polymerization of metastable lactone has been attempted. The metal catalyst has been removed by the metal scavenger and the polymeric product has been isolated and its structure determined by nuclear magnetic resonance (NMR) spectroscopy.