



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

SHORT ABSTRACT OF THESIS

Name of the Student : **ARVIND GUPTA**
Roll Number : 11610713
Programme of Study : Ph.D.

Thesis Title: "**Studies on Stereocomplex Poly(lactic acid) and its Biocomposites**"

Name of Thesis Supervisor(s) : **Dr. Vimal Katiyar**
Thesis Submitted to the Department/ Center : **Chemical Engineering**
Date of completion of Thesis Viva-Voce Exam : **11.09.2017**
Key words for description of Thesis Work : Poly(lactic acid), Stereocomplex, Cellulose microcrystal, Chitosan, Hydroxyapatite, Crystallization kinetics, Thermal degradation, 3D-printing, Lactide, Biobased polymer, Ring opening polymerization.

SHORT ABSTRACT

The current scenario of the world indicates that the consumption of plastics has constantly intensified and laid an impact on the society. However, the disposal of plastics is the prevailing issue of the world which has persuaded the researchers to develop alternatives for a sustainable future. Poly(lactic acid) (PLA) is a biobased plastic which can be considered as promising candidate for replacing petroleum based plastics such as polyethylene, polypropylene, polyethylene terephthalate, etc. PLA has been explored for its applications ranging from biomedical to textiles, agriculture, electronics, and packaging etc. but suffers from some drawbacks such as relatively low glass transition temperature, low heat deflection temperature, lower melting temperature, slow crystallization, lower melt elasticity and relatively poor gas barrier properties. Enhancing the properties of PLA is a major challenge and several methods such as fabricating biocomposite, polymer blending or formation of stereocomplex, etc. have been adopted by the researchers to improve the properties of PLA. PLA can be synthesized by polymerization of lactic acid or its derivative i.e. lactide. Lactic acid is a chiral molecule produced in the form of L-lactic acid, D-lactic acid or racemic lactic acid based on the fermentation reaction pathway. It is desired to produce high molecular weight PLA for several applications which is predominantly produced by ring opening polymerization (ROP) of lactide and the purity of lactide affects the molecular weight of the polymer. Mixing poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) in different ratios, a specific type of polymorph called stereocomplex crystallite is formed which significantly enhances the melting temperature of PLA. Formation of stereocomplex crystallites are also responsible for the enhancement of barrier, mechanical and thermal properties. It has also been reported that low molecular weight PLLA and PDLA in 1:1 ratio can easily form stereocomplex crystallites. In case of high molecular weight i.e. more than 100 kDa,

homocrystallites form along with stereocomplex crystallites which lead to the relatively poor physical properties of end product. Therefore, it is essential to have high content of stereocomplex crystallites to improve the properties without compromising the molecular weight of the end product. The present doctoral work demonstrates the effort to develop a novel process for the production of stereocomplex PLA with high content of stereocomplex crystallites and its characterization. Different biomaterials such as cellulose microcrystals, chitosan and hydroxyapatite have been modified by grafting with PLA chains via in situ ring opening polymerization of lactide and utilized for the development of high molecular weight stereocomplex poly(lactic acid) biocomposites. The grafting of the fillers allows it to be easily dispersed into the polymer matrix which significantly enhances the molecular contact surface area which in turn increases the stereocomplexation as well as the properties of the end product. The utilized biomaterial fillers in the current work have their own diverse properties. Use of cellulose as a filler into the polymer matrix is effective for improving several properties. Cellulose contains large number of hydroxyl groups, present in its molecular structure and surface. Similarly, chitosan is one of the promising materials, which has good oxygen barrier properties, biodegradability and nontoxic nature along with its biocompatibility and antibacterial activity. However, due to its hydrophilic nature, its usage in packaging and engineering applications is limited. Furthermore, hydroxyapatite is a bioactive nontoxic complex form of calcium phosphate which has 60-70% content of mammalian bones. Due to its similarity with mammalian hard tissues, HAP is one of the most investigated synthetic biomaterial. In this thesis, the production of monomer i.e. lactide, its purification and characterization have been discussed. The purification process has been developed to produce highly purified lactide which results in the production of high molecular weight PLA via ROP. The modification of biomaterials via in situ ROP and their use in the production of high molecular weight stereocomplex PLA biocomposites are discussed in detail. The successful modification of the biofillers has been carried out and their presence in the PLA matrix has significantly improved the content of stereocomplex crystallites which in turn significantly enhance the properties of biocomposites. Improvement in the properties such as gas barrier, thermomechanical and thermal properties could be achieved by enhancing the stereocomplexation in the matrix which may be the result of uniform dispersion of the filler. From the processing point of view, a detailed crystallization kinetics and thermal degradation kinetics of the stereocomplex PLA and its biocomposite have been demonstrated.