

Bioproduction of polyesters

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Polyesters are polymers comprising of repeating ester groups as chain structure backbone, being the most popular biodegradable polymers. Many studies related with the synthesis of aliphatic and aromatic polyesters using chemical processes have been carried out [1]. Poly (ethylene glutarate) (PEG), Poly(ethylene malonate) (PEM), Poly(ethylene phthalate) (PEP) are attractive polyesters by virtue of their easiness in synthesis and widely diversity of applications such as textile manufacturing, microelectronics, bioprocessing, food packaging as well as in bio medical like surgical threads, contact lenses, supporting material in bone repairing, treat air leaks in lung injury. The chemical synthesis of these polyesters requires harsh conditions like high temperature and pressure, long reaction times and costly downstream processing. Many strategies such as the designing of recyclable catalysts, alteration of reaction conditions and the use of biocatalysts have been implemented to overcome these problems and make them green and environmentally friendly processes [2]. Recently, a new approach for synthesizing these type of polyesters has been developed by enzyme-catalysed polymerization. Potentially a solvent-free enzymatic system can offer better processing conditions without further complex purification process. The use of solid immobilized enzymes in solvent free systems where the reactants are the solvents itself might yield slow reaction rates due to the limiting diffusion between reactants and mass transfer limitations. The use of ultrasound might also contribute to push the reaction forward due to the cavitation effects, such as increased local temperature and pressure as well as the generation of micro level mixing and turbulence conditions. Template-assisted synthesis is also considered to study the effect of PEG addition, free or linked to the catalyst.

Herein, Poly(ethylene glutarate) was synthesized by reaction of equimolar amount of diethyl glutarate and ethylene glycol with 2 or 20% (w/v) of native and PEGylated enzymes (cutinase from *Fusarium solani pisi*, immobilized lipase B from *Candida Antarctica* and lipase from *Thermomyces Lanuginosus*). The mixture was placed in an ultrasonic bath for 1 or 2h and then under vacuum until 7h. The reaction products were characterized by NMR spectroscopy, Maldi-TOF mass spectrometry, FT-IR, differential scanning calorimetry (DSC) and thermogravimetric analysis (Tga).

- [1] Korley, JN, Yazdi S, McHugh K, Kirk J, Anderson J, Putnam D, One-step synthesis, biodegradation and biocompatibility of polyesters based on the metabolic synthon, dihydroxyacetone, *Biomaterials*, 98, 41-52, 2016.
- [2] Thomas CM, Stereo controlled ring-opening polymerization of cyclic esters: synthesis of new polyester microstructures, *Chemical Society Reviews*, 39, 165-173, 2010.