Recent Progress in Ring-Opening Polymerization of ε-Caprolactone and derivatives

Poly ε-caprolactone (PCL) and polylactides (PLA) are thermophlastics with quite unusual properties of polymer miscibility (PCL), biocompatibility and (bio)degradability. They are thus environmentally friendly polymers and they have potential in biomedical applications.

e-Caprolactone (seven membered cyclic ester) and lactide (cyclic diester of lactic acid) are polymerized in a controlled fashion according to a coordination insertion mechanism initiated by Al, Sn and rare-earth alkoxides. Chains of well defined molecular weight and macromolecular architecture, with specific end-groups if required, can accordingly be synthesized. In addition to this macromolecular engineering, physico-mechanical properties of PCL and PLA can be changed by the incorporation of few wt% of layered silicates. These nanocomposites can be prepared by melt intercalation of preformed polyester chains or by dispersing the clay in the monomer which is then polymerized. The "in situ" ring-opening polymerization (ROP) can be conducted in the presence of clay premodified by ammonium cations bearing substituents inert towards the active species or able to initiate thethered chains. All the situations from non-intercalated to completely exfoliated clays are observed, which controls a series of properties, including permeability, mechanical and thermal properties.

Interestingly enough, ROP of ε-CL and LA can be carried out successfully in supercritical CO_2. The polymerization control is maintained, monomer and metal residues can be extracted, the polymer can be expanded or collected as spherical particles. Nanocomposites of PCL have been prepared in $scCO_2$ and expanded. Modification of the PCL rheology by nanofiller is essential to the successful foaming.

PLA foams have also been filled with Bioglass in order to prepare bioactive composite scaffolds for bone tissue engineering.

Finally, surface of metals and glassy carbon has been coated by strongly adhering film of PCL and functionalized polymers for multifold purposes.