SYNTHESIS OF POLYLACTIDE-GRAFT-MALEIC ANHYDRIDE VIA FREE RADICAL INITIATION IN SUPERCRITICAL CARBON DIOXIDE

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One of the most popular bio-based polymers on the market today is polylactide (PLA). Although PLA is bio-based, biodegradable, produced on a large scale, and able to be processed by traditional polymer processing equipment, its widespread use is limited by its relatively poor mechanical properties. PLA possesses a high tensile modulus, but low elongation and toughness. It is an inherently brittle material and therefore a poor choice for flexible packaging applications in its virgin form. PLA can be melt blended with more flexible polymers to increase its suitability for a wider range of applications, but due to their high molecular weight and viscosity, polymers are rarely miscible with each other. Immiscible polymer blends cause premature separation of polymeric phases, discontinuity of mechanical and thermal properties, and shortened service life. Graft copolymers can serve as compatibilizers between immiscible polymer blends to improve their miscibility and subsequent mechanical properties.

In this work, polylactide-graft-maleic anhydride (PLA-g-MA) will be synthesized with the ultimate objective of incorporating this graft copolymer as a compatibilzer into bio-based polymer blends with PLA as the main phase. PLA-g-MA will be synthesized in a stainless steel batch reactor in the presence of supercritical carbon dioxide ($scCO_2$). ScCO2 is an effective medium for polymerization because while most polymers do not dissolve, they tend to swell in scCO2, allowing for diffusion of reactive monomer into the swollen polymer. In addition, the density of the CO2 can be easily tuned by changing pressure and/or temperature, and the reaction can take place under ideal conditions without the harsh organic solvents utilized in solution grafting or high temperatures employed in molten state grafting.

In this study, the amount of initiator and MA will be kept constant at 2.5 wt% and 10 wt%, respectively, and the scCO2 density will be held at 300 kg/m^3. Azobisisobutyronitrile (AIBN) and Benzoyl Peroxide (BPO) will be used as the free radical initiators, and reactions will be carried out at three different temperatures for each of two initiators studied.

After the grafting reaction has taken place, the samples will be purified using Soxhlet extraction in methanol to remove excess monomer and spent initiator and Fourier Transform Infrared (FTIR) and Proton (^1H) Nuclear Magnetic Resonance (NMR) spectroscopy will be utilized to ensure that grafting has taken place and to determine the grafting level. The optimum reaction temperature and initiator will be determined based on these results.