Summary

In the recent years, the concerns related to the environmental issues stimulated an increasing interest towards the application of biodegradable polymers. However, the use of these renewable resources, in alternative to the conventional petrochemical derived products, has some disadvantages such as limited thermo-mechanical properties. A possible and effective method to overcome some biopolymers limitations is the development of bio-based polymer blends.

Particularly, the purpose of this PhD dissertation is the study of compatibilized biopolymer blends: different strategies of compatibilization derived from a detailed state of the art were discussed. The aim is to develop fully bio-based materials with advanced thermo-mechanical and mechanical properties overcoming the limitations related to the immiscibility of the biopolymer phases. Concerning the experimental trials, the use of natural surfactants, the use of nanoparticles connected to an accurate study of the influence of process parameters during melt compounding and, finally, the use of a third biopolymer phase were employed as methods in order to obtain materials with improved interfacial adhesion between the immiscible phases. In particular, the study was focused on blends composed by poly(lactic-acid) (PLA) as continuous phase and different biopolymers as dispersed phases. The choice of using PLA is correlated to the well-known biocompatibility and biodegradability of this biopolymer but, especially, to its easy processability that allows the use of existing polymer-processing equipment and techniques for petrochemical-derived products.

Morphological investigation and detailed studies of thermal, thermo-mechanical and rheological properties are reported.

Particularly, an innovative use of non-ionic surfactants has been tested in a model system based on poly(lactic-acid) (PLA) and low-density polyethylene (LDPE). Subsequently, the effectiveness of the proposed strategy was evaluated for fully bio-based PLA/ poly-hydroxy butyrate (PHB) blends. In addition, for the bio-based blends a further compatibilization system based on solid non-ionic surfactants, named Synperonic (Syn), was used. Morphological analyses of the compatibilized blends indicated that in both compatibilized systems a certain grade of compatibility and improved interfacial adhesion between phases, as compared to

the non-compatibilized blend, were achieved. Finally, a remarkable increase of the elastic modulus values was obtained for the compatibilized blends as compared to the pure counterparts, with a consequent significant enhancement of the heat distortion temperature values which allows to obtain a wider application working range of these materials.

A very important aspect, broadly studied in this PhD dissertation, is the influence of the process parameters on the final properties of the blends by knowing that their microstructure is closely related to the melt blending process and the conditions under which the process takes place. The results of the characterizations of PLA/PHB blends processed with different screw configurations of a co-rotating twin screw extruder, flow rate and screw speed are reported. In addition, nanofilled PLA/PHB blends with nanoclays were processed by varying the screw configuration and the screw speed. In this case, XRD analyses, SEM observations and rheological characterization were exploited to infer the coupled effect of the process parameters and nanoclay presence on the microstructure of the filled blend. Preliminary thermodynamic calculations allowed predicting the preferential localization of the nanoclay in the interfacial region between the polymeric phases. The relaxation mechanism of the particles of the dispersed phase in nanofilled blend processed, by rheological measurements, is not fully completed due to an interaction between polymer ad filler in the interfacial region with a consequent modification of the blend morphology and, specifically, a development of an enhanced microstructure. Therefore, by varying the screw configuration, particularly the presence of backflow and distribution elements, high shear stresses are induced during the processing able to allow a better interaction between polymers and clay.

Finally, another compatibilization strategy reported in the work thesis was the introduction of a further biopolymer phase in a binary immiscible blend. In particular, poly-butylene succinate (PBS) was used as ductile phase in order to enhance the elongation at break of the PLA/PHB brittle blend. The ternary systems reported ductile behaviour with elongation at break increased up to 297% overcoming the brittleness typical of PLA and PHB polymers.