CHAPTER 5

Summary
And
Conclusions
The synthesis of StTh and StCn as well as their use in development of blends with commercial plastics has not been reported in literature.

From these studies following conclusions are drawn.

1. The esterification of starch leads to an increase in the thermoplastic character, thermal stability and hydrophobicity, thus making it favorable for blending with LDPE. Morphology reveals that on esterification, the surface of starch granule becomes somewhat rough. This roughness brings about increased adhesion between starch and the LDPE matrix due to improved state of interface.

2. Morphology also reveals a highly crystalline nature of starch phthalate, which was confirmed by a sharp melting point.

3. The degree of substitution of StAc, StTh and StCn was found to be 2.5, 2.3 and 1.8 respectively. Biodegradation studies in culture medium showed that the starch derivatives show lower biodegradability than native starch. The possible degradation pathway of starch ester may be due to the esterase and amylase enzymes secreted by the microbes. The ester bond is cleaved by the esterase releasing free acid and starch, and amylase acts on starch to produce reducing sugars.

4. The substitution of starch by StAc / StTh in the blends of LDPE showed an increase in mechanical and thermal properties. Morphology of binary LDPE / StAc and LDPE / StTh blends showed greater adhesion between two phases compared to binary LDPE / starch blends. This desirable improvement with replacement of starch by StAc / StTh at all blend compositions indicates that there is a better adhesion between derivatised starch and hydrophobic LDPE compared to native starch.
5. An interesting feature is the greater soil degradation of LDPE/modified starch blends, although native starch showed higher degradation than starch derivative in the culture medium. SEM analysis of the biodegraded films indicated surface growth and colonization of both bacterial and fungal culture.

6. Comparison of the binary blends of StAc, StTh and starch showed that tensile strength, elongation at break and impact properties follow the trend PE/StAc > PE/StTh > PE/starch. Thus the use of starch esters in place of starch leads to a definite improvement in mechanical properties. Among the two starch esters, StAc appears to be a better substitute than StTh. This can be attributed to the highest degree of substitution and hence enhanced hydrophobicity of StAc leading to increased adhesion with the LDPE matrix.

7. Viscometry of the blend solutions of starch cinnamate and starch acetate was carried out in 1,4-dioxane. The relative and intrinsic viscosity data showed that StCn was found to be incompatible with nonpolar commercial polymer polystyrene but compatible with polar polymers like PMMA, PVC and SAN. Poly (vinyl chloride), though compatible with StCn, was observed to be incompatible with StAc. The density and ultrasonic velocity measurements of the blend solutions also supported these observations.

8. The compatibility behavior of StCn blends was also examined in three different solvents; 1,4-dioxane, DMF and THF. It was observed that nature of solvent did not have a significant effect on the compatibility behavior.

9. Prediction of compatibility of blends on the basis of theoretical parameters showed that, the heat of mixing data supports the
experimental results. However, the polymer-polymer interaction parameters such as $\Delta B$, $\Delta b$, $\mu$ and $\alpha$ were in conflict with the experimental results. This may be because one component of the present blends systems is starch derivative. As the interactions considered in the above parameters are generally for a pair of synthetic polymers, they may not be suitable in the present case.

10. Morphology of solution cast films of blends showed that etched films showed removal of uniformly distributed dispersed phase in all the blends except PMMA / StCn blends.

11. The soil degradation of solution cast films containing upto 30 % StCn, showed that the percentage weight loss increased with increasing content of starch cinnamate in all the blends. The blends containing 30 % StCn showed relatively more rapid and substantial weight loss. This may be attributed to the greater accessibility of starch to microorganisms at this composition. The percentage weight loss of compatible blends was found to be lower than that of the incompatible blends.

The overall observation is that upto about 15 to 20 % of modified starch can be incorporated into LDPE for introduction of partial degradability without much compromise in the mechanical strength. Thus the blends under study show better mechanical, thermal as well as morphological properties than the blends with native starch alone and also show potential as biodegradable polymers. Further, the blends shown to be compatible by solution techniques can also be made suitable for the application purpose. The technique of solution blending can be used for the prediction of compatibility of blends.

The approach described in the present investigation can be exploited to develop a commercially viable means of developing environment friendly materials.
density polyethylene has occupied a prominent position as commodity plastic because of its growing commercial application. However, because of its non-biodegradable nature it has created serious environmental problems. Hence, its use is being restricted. An efficient way of overcoming this problem is development of partially biodegradable LDPE / starch blends. Similarly some engineering plastics can also be made partially degradable by blending with starch in such a way that the mechanical strength is retained and biodegradability is induced. But starch because of its highly hydrophilic nature and crystallinity is incompatible with most of these commercial polymers.

Hence its original properties need to be modified before it can be used for blending. Therefore we have synthesized starch acetate (StAc) and starch phthalate (StTh) using the respective acid chloride or anhydride. They were thoroughly characterized for degree of substitution, spectral and thermal properties, morphology and biodegradability. These starch derivatives were used for the development of LDPE / starch blends.

Several blends of different compositions but at similar processing conditions were prepared by melt extrusion technique using twin-screw extruder. The blends were thoroughly characterized for their mechanical, thermal morphological and biodegradable properties.

Another derivative, starch cinnamate (StCn), had lower thermal stability than native starch and hence was not used for melt blending, rather it was used to develop blends with PVC, PMMA, PS and SAN in solution. The blends were prepared with different compositions and blend compatibility was predicted through viscosity, density and ultrasonic velocity measurements. Experimental results were correlated with the theoretical parameters used for the prediction of blend compatibility in solution.