

Bio Degradability test of blend of PLA and modified starch

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ABSTRACT

Blends were prepared from poly(lactic acid) (PLA) and thermoplastic starch (TPS) to study component interactions, structure and properties. Starch was plasticized with cashew nut shell oil (CNSL). The results unambiguously showed that the interaction of the two components is weak. The investigation of the possible partitioning of CNSL in the two phases indicated that most of the plasticizer is located in the TPS phase. Thermodynamic modeling predicted some dissolution of PLA in TPS which was assisted by the presence of the plasticizer, but TPS did not dissolve in PLA at all. No tangible proof was found for the formation of CNSL rich phase in TPS, the relaxation transition assigned to this phase was rather explained with the movement of smaller structural units of starch molecules. Weak interfacial adhesion does not allow stress transfer through the interface resulting in poor strength and small deformation.

Key words: thermoplastic starch, molecular modeling, thermodynamics,

1. INTRODUCTION

In recent years the importance of biopolymers increases continuously and further growth is forecasted in their use in the future. However, besides the obvious environmental advantages of these materials, they have some deficiencies as well, like inferior properties compared to commodity polymers, poor processability, water sensitivity, etc. To overcome these drawbacks biopolymers are frequently modified, often by blending. The mixing of poly(lactic acid) (PLA) and thermoplastic starch would combine the advantages of the two polymers by maintaining complete biodegradability and resulting in a relatively cheap material [1-5]. However, the two polymers are immiscible, heterogeneous blends form upon their mixing, and the statements about the compatibility of TPS and aliphatic polyesters are often contradictory. Avérous and Fringant [6, 7] found dissimilar compatibility in various starch/aliphatic polyester blends. In a further study Martin and Avérous [8] claimed low level of compatibility in PLA/TPS blends, but in another part of the same paper they state that changes in T_g indicate some interaction between TPS and PLA. The degree of compatibility claimed varies in a wide range depending on blend components and the authors of the paper. Maetal. [9, 10], for example, found complete immiscibility in PLA/TPS blends when the plasticizer was CNSL, while good compatibility, when DCP was used. However, the statements on compatibility or miscibility are almost invariably qualitative in nature and based on the observation of SEM micrographs, changes in T_g or mechanical properties, but rarely on thermodynamic considerations. Poor compatibility of the components is also indicated by attempts to improve interactions by preparing hybrid blends[11], adding amphiphilic molecules [12] or a coupling agent [13]. Another interesting question that is never discussed or even mentioned in relation with TPS blends is the role of the plasticizer. Although many papers have been published on TPS plasticized with the most diverse compounds, on their efficiency and on the structure formed, TPS is treated as a single, homogeneous material in blends, in spite of the fact that TPS plasticized with glycerol was claimed to phase separate above a certain plasticizer content [6, 7, 14-17]. The distribution of a third material, e.g. the aliphatic polyester, in a two phase polymer, TPS, can be quite complicated, several structures may form and must be considered. Moreover, the plasticizer is a small molecular weight substance which is quite mobile at the temperature of processing, but also under ambient conditions. Although originally it is located in starch, it may diffuse into the other polymer during processing and partition between the two polymer components. Although Maetal. [9, 10] claimed improvement in compatibility upon the use of formamide compared to glycerol, they did not explain the effect or its mechanism either. In view of these questions, the goal of this work was to estimate interactions in PLA/TPS blends by thermomechanical analysis [18-20] and thermodynamic modeling, study the role and

partitioning of the glycerol plasticizer in the components and determine the structure and properties of the blends in a wide composition range.

2. Experimental

2.1. Materials

PLA pellet (2003D grade) by NatureWorks . It is transparent polymer with a glass transition temperature of 58–60°C and a density of 1.24 g/cm³, as reported by the manufacturer. It was vacuum dried at 80 °C for at least 8 h before use. Corn starch was purchase from santosh Food Products Public Company Limited . which was dried in vacuum for 24 h at 100 °C before use. Cashew nut shell oil was supplied from Shivam cashew industry. Maleic anhydride (≥98% purity) produced by Sigma Aldrich, dicumyl peroxide (98% purity).

2.2 Synthesis of MA-grafted starch

The MA-grafted starches were prepared in a three-neck flask equipped with a Dean-Stark distilling receiver, a condenser and a mechanical agitator. Starch and MA were first charged into the flask,. The reaction temperature was then brought up to 130 °C with the agitation. The reaction was kept at this temperature for 1 h and then cooled to room temperature. The final product was dried in vacuo at 80 °C for 24 h and then kept in a desiccators. This step is called master batch preparation.

2.3. Master batch formulation:

MATERIAL	PHR
STARCH	72.115
CNSL	24.038
MA	2.884
DCP	0.961
TOTAL	100

2.4. Blends

The PLA/starch, PLA/CNSL, PLA/CNSL/starch, and PLA/CNSL/MAgraft- starch (MGST) blends were melt-blended in a SJSZ-10A miniature twin-screw extruder with 40 rpm at 175 °C for 10 min. The extrudants were then injection molded into the standard testing bars with the barrel temperature of 200 °C, mold temperature of 45 °C, an injection pressure of 5 MPa and a cycle time of 30 s. In the PLA/starch blends, the content of starch was 30 wt.%, 40 wt.% and 50 wt%, respectively. Blends of PLA\starch were prepared in 3 batches, called final batches.

2.5. Formulation of final batches

MATERIAL	BATCH 1	BATCH 2	BATCH 3	TOTAL PHR
PLA (PHR)	70	60	50	100

MASTER BATCH (PHR)	30	40	50	100
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3. TESTING

3.1. Hot Water Degradation

Three samples were allowed to degrade in hot water at about 60⁰ C temp. for 96 hrs. by using heating mental and flask and Petri dish.

Material	Initial wt. (gm)	Final wt. (gm)	% degradation
B ₁	8.02	3.92	25.12
B ₂	8.02	3.19	60.22
B ₃	8.02	2.26	71.82

3.2. Soil Degradation

Three samples were allowed to degrade in soil for 17 days by buried the samples in 1” deep in soil, the results obtained are as follows.

Material	Initial wt. (gm)	Final wt. (gm)	% degradation
B ₁	8.66	8.09	6.59
B ₂	8.60	7.92	7.90
B ₃	8.02	7.20	10.10

4. Conclusion

From the testing results one can conclude that degradation is done on higher percentage with respect to soil degradation, and as we proceed from batch 1 to batch 3 the degradation percentages increases because the ratio and percentage of modified starch is been increasing, and it is clear that starch is more and easily degradable than PLA so as we proceeds from batch 1 to batch 3 degradation results increases.

5. References

1. Chakraborty A, Sain M, Kortschot M, and Cutler S. Dispersion of wood microfibers in a matrix of thermoplastic starch and starch-poly(lactic acid) blend. *Journal of Biobased Materials and Bioenergy* 2007;1(1):71-77.
2. Shirai MA, Grossmann MVE, Mali S, Yamashita F, Garcia PS, and Müller CMO. Development of biodegradable flexible films of starch and poly(lactic acid) plasticized with adipate or citrate esters. *Carbohydrate Polymers* 2013;92(1):19-22.
3. Teixeira ED, Curvelo AAS, Correa AC, Marconcini JM, Glenn GM, and Mattoso LHC. Properties of thermoplastic starch from cassava bagasse and cassava starch and their blends with poly (lactic acid). *Industrial Crops and Products* 2012;37(1):61-68.
4. Huneault MA and Li H. Morphology and properties of compatibilized polylactide/thermoplastic starch blends. *Polymer* 2007;48(1):270-280.
5. Li H and Huneault MA. Comparison of sorbitol and glycerol as plasticizers for thermoplastic starch in TPS/PLA blends. *Journal of Applied Polymer Science* 2011;119(4):2439-2448.

6. Avérous L, Moro L, Dole P, and Fringant C. Properties of thermoplastic blends: starch–polycaprolactone. *Polymer* 2000;41(11):4157-4167.
7. Avérous L and Fringant C. Association between plasticized starch and polyesters: Processing and performances of injected biodegradable systems. *Polymer Engineering & Science* 2001;41(5):727-734.
8. Martin O and Avérous L. Poly(lactic acid): plasticization and properties of biodegradable multiphase systems. *Polymer* 2001;42(14):6209-6219.
9. Wang N, Yu J, Chang PR, and Ma X. Influence of formamide and water on the properties of thermoplastic starch/poly(lactic acid) blends. *Carbohydrate Polymers* 2008;71(1):109-118.
10. Wang N, Yu J, and Ma X. Preparation and characterization of compatible thermoplastic dry starch/poly(lactic acid). *Polymer Composites* 2008;29(5):551- 559.
11. Zhang K, Mohanty AK, and Misra M. Fully biodegradable and biorenewable ternary blends from polylactide, poly(3-hydroxybutyrate-co-hydroxyvalerate) and poly(butylene succinate) with balanced properties. *ACS Applied Materials & Interfaces* 2012;4(6):3091-3101.

